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**SCIENTIFIC CRITERIA DOCUMENT
FOR DEVELOPMENT OF
PROVINCIAL WATER QUALITY
OBJECTIVES AND GUIDELINES**

ALUMINUM

SEPTEMBER 1988



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EXECUTIVE SUMMARY

Several sources of aluminum account for ambient concentrations in aquatic ecosystems in Ontario. These include natural sources resulting from mineral weathering, as well as anthropogenic sources such as industrial processing, and alum treatment of water for drinking, sewage treatment and pulp and paper processing.

Aluminum can combine with a number of organic and inorganic anions to form simple complexes or very large complex molecules in suspension. The dominant forms of aluminum found in a given waterbody will be a function of the competing anions and aquatic parameters such as pH, alkalinity, hardness, and DOC. pH and DOC have been identified as the most significant parameters governing the behaviour of aluminum ions in solution. The nature of the aluminum ion complex will influence aquatic toxicity.

Analytical procedures can now identify and measure some forms of aluminum that are toxic to aquatic life in low pH regimes. Inorganic aluminum, particularly inorganic monomeric aluminium (IMAL), is the form considered to be most toxic in acid stressed environments, organic aluminum being relatively non toxic. However, at mildly acidic pH values where aluminum solubility is minimal, supersaturated solutions of inorganic aluminum also appear to be toxic. At pH values greater than 6.5 the toxic forms of aluminum have not been identified. The organic and inorganic forms of aluminum are difficult to separate by current routine analytical procedures.

Toxicological information from a wide range of laboratory and field studies has been assessed for use in this report. Although there is a large amount of information available for total aluminum toxicity in a wide variety of species, relevant data for the pH range 4.5 to 6.5 showing toxicity of inorganic aluminum alone are almost entirely from studies on fish. Data from a broader spectrum of species have been used in the pH range 6.5 to 9.5.

Three Provincial Water Quality Guidelines have been developed for aquatic environments with pH values from 4.5 to 9.0. Two are numerical guidelines, one is narrative. All are intended for samples free of any clay fraction (see Appendix I for analytical procedures). They are:

- *1. AT pH 4.5 to 5.5 THE GUIDELINE IS 0.015 mg/L BASED ON INORGANIC MONOMERIC ALUMINUM MEASURED IN CLAY-FREE SAMPLES.
- 2. AT pH >5.5 TO 6.5 NO CONDITION SHOULD BE PERMITTED WHICH WOULD INCREASE THE ACID SOLUBLE INORGANIC ALUMINUM CONCENTRATION IN CLAY-FREE SAMPLES TO MORE THAN 10% ABOVE NATURAL BACKGROUND CONCENTRATIONS FOR WATERS REPRESENTATIVE OF THAT GEOLOGICAL AREA OF THE PROVINCE THAT ARE UNAFFECTED BY MAN-MADE INPUTS.
- *3. AT pH >6.5 to 9.0 THE GUIDELINE IS 0.075 mg/L BASED ON TOTAL ALUMINUM MEASURED IN CLAY-FREE SAMPLES

*IF NATURAL BACKGROUND ALUMINUM CONCENTRATIONS IN WATER BODIES UNAFFECTED BY MAN-MADE INPUTS ARE GREATER THAN THE NUMERICAL GUIDELINES (Nos. 1 & 3) NO CONDITION IS PERMITTED THAT WOULD INCREASE THE ALUMINUM CONCENTRATION IN CLAY FREE SAMPLES BY MORE THAN 10% OF THE NATURAL BACKGROUND LEVEL.

These guidelines are for the protection of all forms of aquatic life, recreational purposes, and aesthetic values. They are not drinking water guidelines.



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SOMMAIRE

Les concentrations d'aluminium dans les écosystèmes aquatiques de l'Ontario proviennent de plusieurs sources. Il y a d'abord les sources naturelles, comme l'érosion, puis les sources anthropiques, comme les activités industrielles, le traitement de l'eau à l'alun en vue de la rendre propre à la consommation, le traitement des eaux d'égout et la fabrication de pâtes et papiers.

L'aluminium forme des molécules en suspension simples ou complexes en se combinant à un certain nombre d'anions organiques et d'anions inorganiques. Les formes d'aluminium qui dominent, dans un cours d'eau donné, dépendent des anions et de paramètres aquatiques, tels le pH, l'alcalinité, la dureté et le COD (carbone organique dissous). On a constaté que le pH et le COD étaient les paramètres ayant le plus d'importance dans le comportement des ions d'aluminium en solution. La nature de ceux-ci influe sur la toxicité de l'eau.

On peut désormais, grâce aux analyses, isoler et mesurer quelques-unes des sortes d'aluminium qui sont toxiques pour la faune et la flore des milieux aquatiques à faible pH. Ainsi, les monomères inorganiques d'aluminium sont très toxiques dans un environnement perturbé par l'acide, tandis que les monomères organiques le sont peu. Toutefois, il semble que, dans un milieu légèrement acide où la solubilité de l'aluminium est minime, les solutions sursaturées de monomères inorganiques soient aussi toxiques. On n'a pu isoler de formes toxiques d'aluminium lorsque le pH est supérieur à 6,5. Signalons que les analyses couramment employées permettent difficilement de séparer les monomères organiques ou inorganiques.

Le présent rapport renferme aussi des renseignements toxicologiques provenant d'un grand nombre de recherches effectuées en laboratoire et sur le terrain. Bien qu'il existe beaucoup de renseignements sur la toxicité de l'aluminium total pour diverses espèces, les données se rapportant exclusivement à la toxicité des monomères inorganiques d'aluminium à un pH variant de 4,5 à 6,5 sont tirées en majorité d'analyses sur les poissons. Dans le cas d'un pH allant de 6,5 à 9,5, on a utilisé des données sur un large éventail d'espèces.

Le Ministère a élaboré trois lignes directrices sur la qualité de l'eau dans les milieux aquatiques dont le pH va de 4,5 à 9,0. Deux d'entre elles imposent un seuil numérique, tandis que la troisième est de nature explicative. Toutes ont été élaborées pour des échantillons ne contenant pas de morceaux d'argile (voir à l'appendice I les méthodes d'analyse). Les voici :

1. pH DE 4,5 À 5,5. LE SEUIL A ÉTÉ FIXÉ À 0,015 MG/L, D'APRÈS LA CONCENTRATION DE MONOMÈRES INORGANQUES D'ALUMINIUM MESURÉE DANS DES ÉCHANTILLONS SANS MORCEAUX D'ARGILE.
2. pH DE >5,5 À 6,5. IL FAUT ÉVITER QUE LA CONCENTRATION DE MONOMÈRES INORGANQUES D'ALUMINIUM SOLUBLES DANS L'ACIDE DANS DES ÉCHANTILLONS SANS MORCEAUX D'ARGILE DÉPASSE DE PLUS DE 10 % LES CONCENTRATIONS DE FOND NATURELLES POUR LES EAUX D'UNE RÉGION GÉOLOGIQUE DONNÉE DE LA PROVINCE NON TOUCHÉES PAR L'ACTIVITÉ HUMAINE.

- *3. PH DE >6,5 À 9,0. LE SEUIL A ÉTÉ FIXÉ À 0,075 MG/L, D'APRÈS LA CONCENTRATION D'ALUMINIUM TOTAL, MESURÉE DANS DES ÉCHANTILLONS SANS MORCEAUX D'ARGILE.

* SI LES CONCENTRATIONS DE FOND NATURELLES DES EAUX NON TOUCHÉES PAR L'ACTIVITÉ HUMAINE SONT SUPÉRIEURES AUX SEUILS NUMÉRIQUES DES LIGNES DIRECTRICES 1 ET 3, ON DOIT EMPÊCHER TOUTE SITUATION POUVANT FAIRE EN SORTE QUE LA CONCENTRATION D'ALUMINIUM DANS LES ÉCHANTILLONS SANS MORCEAUX D'ARGILE DÉPASSE DE PLUS DE 10 % LES CONCENTRATIONS DE FOND NATURELLES.

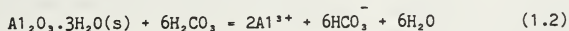
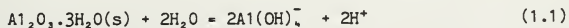
Ces lignes directrices sont destinées à protéger la flore et la faune aquatiques, les usages récréatifs des cours d'eau ainsi que les valeurs esthétiques. Elles ne visent nullement la qualité de l'eau potable.

1.0 SOURCES

1.1 Natural Sources

Aluminum is the third most abundant element making up about 8% of the earth's crust. It occurs in many silicate minerals such as feldspars, feldspathoids, micas, and amphiboles. The aluminum ion has four-fold coordination with oxygen and can substitute for silicon in mineral lattices. In six-fold coordination, crystal sites similar to those occupied by magnesium and iron can be duplicated (Hem, 1970). Aluminum hydroxide, in the form of gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}(\text{s})$), is a common mineral, while the sulphate and fluoride species are less common. Clays, present in most natural waters, are composed of alternating structural layers of aluminum oxides and/or hydroxides and silicon oxides (Hem, 1970).

Weathering processes involve mechanical fragmentation through thermal fluctuations and fracturing, and abrasion of surfaces by solid particles carried by wind, water or ice. Particle sizes are reduced and surface areas are increased to the greater advantage of chemical interactions. Water, carbon dioxide and organic acids represent the major natural chemical weathering agents. The reactivity of these agents and the release of ionic constituents from the parent materials is determined by the solubility of the species and the pH of the aqueous solution. Examples of typical weathering reactions involving gibbsite are:



While weathering contributes to the fragmentation of rock forms, it also contributes to the formation of sedimentary structures. Thus, a cycling of elements can take place through the weathering process. Aluminum, as one of the most abundant elements in this cycling process, is present in relatively high concentrations in igneous rock (e.g., granite 13% and basalt 16%) as well as in

most sedimentary rocks (e.g., shale 15%, sandstone 5% and limestone 1%) (from Bonstrom, 1972). The predominance of aluminum persists or is even concentrated in soils originating from these same rock types (basalt 31%, granite 26%, limestone 22%) (from Bonstrom 1972)

Through geologic time, the earth's atmosphere has included small amounts of the gases Cl_2 , SO_2 and H_2S resulting from volcanic activity, which tend to acidify precipitation. The relatively recent advent of industrialization and fossil fuel combustion has substantially increased the availability of SO_2 and NO_x (Harvey et al., 1981). This has further increased the acidity of precipitation, and enhanced the dissolution rate of aluminum from rock and soils, resulting in higher loadings of the element into watersheds and aquatic systems (Cronan and Schofield, 1979).

1.2 Industrial Sources

1.2.1 Mining and Smelting

Bauxite or aluminum ore is composed of about 55% aluminum oxide and less than 7% silica. Although the ore is not indigenous to Canada, there are aluminum smelting operations in Quebec and British Columbia. There are no such operations in Ontario.

1.2.2 Commercial Products

Aluminum is used as a metal in fabrication or construction because of its unique, weight-to-strength, electrical and thermal conductance properties.

Alum or aluminum sulphate is the most common commercial chemical product containing aluminum and is manufactured by reaction of aluminum with sulphuric acid. The reaction solution is washed countercurrently to remove waste and directed to an open heated evaporator. The concentrated liquor is poured into flat pans

where it cools and solidifies. The solid alum is broken and ground to size. Annual Canadian production capacity is nearly 270,000 tonnes (Shockett, 1984).

Almost 50% of the alum produced is used in the pulp and paper industry for resin sizing, pitch control, pH control and process water treatment. About 30% of the alum is used to control pH and precipitate suspended solids and phosphorus in municipal water and sewage treatment operations. The remaining alum is exported or used in pigment and synthetic crude production.

Aluminum chloride has found application in the petroleum and organic chemical industry principally as a catalyst in production. The two Canadian producers, St. Clair Chemical Limited and Welland Chemical of Canada Limited, are located in Sarnia. Aluminum chloride is produced by the reaction of gaseous chlorine on molten aluminum. Chlorine is introduced below the surface of the aluminum, and the sublimed product is collected by condensation. Production capacity was not determined.

Several other aluminum-containing organic and inorganic chemicals are manufactured, but production capacity information is not available.

1.2.3 Major Release Points

Aluminum that is smelted will be largely contained in its elemental form and protected from release by the nature of the construction, transportation, packaging, electrical and machinery manufacturing uses. Losses of aluminum sulphate from the pulp and paper industry will be limited by quality control programs to maintain consistent sizing characteristics. However, applications in water treatment represent the greatest potential for anthropogenic losses of aluminum to receiving waters. A summary of total quantities, as elemental aluminum, that have been used in water-related industrial applications over the last four years are outlined in Table 1.1. Volumes are expected to increase 4.5% annually over the next several years.

TABLE 1.1 VOLUME OF ELEMENTAL ALUMINUM USED IN CANADA¹

Use	Quantity Used (1,000 tonnes)			
	1980	1981	1982	1983
Pulp and Paper	8.7	8.5	8.2	8.5
Municipal (drinking water/sewage)	4.4	4.5	4.7	5.4
Miscellaneous	1.5	1.5	1.3	1.4
TOTAL	14.6	14.5	14.2	15.3

¹Based on Shockett (1984).

2.0 ALUMINUM CHEMISTRY IN AQUEOUS SOLUTIONS

Though aluminum is ubiquitous in the earth's crust, concentrations of dissolved aluminum are generally low in most circumneutral waters due to the low solubility of natural aluminum minerals. Stumm and Morgan (1980) report a median value of 0.011 mg total Al/L for groundwater; while in Ontario lakes, total aluminum levels can range from a few $\mu\text{g/L}$ to over 300 $\mu\text{g/L}$ (see Fig. 4.1).

Aluminum in aqueous solutions is characterized by the reaction of aluminum hydroxide with water and may be present in a monomeric or polymeric form. A monomer consists of one aluminum ion, while a polymer consists of several aluminum ions connected by hydroxyl groups. Certain properties of aluminum in solution are:

- o it is amphoteric (can behave as a base or an acid);
- o it forms complexes with organic and inorganic substances in the water; and
- o it tends to polymerize (simple monomers combined to form large complex molecules).

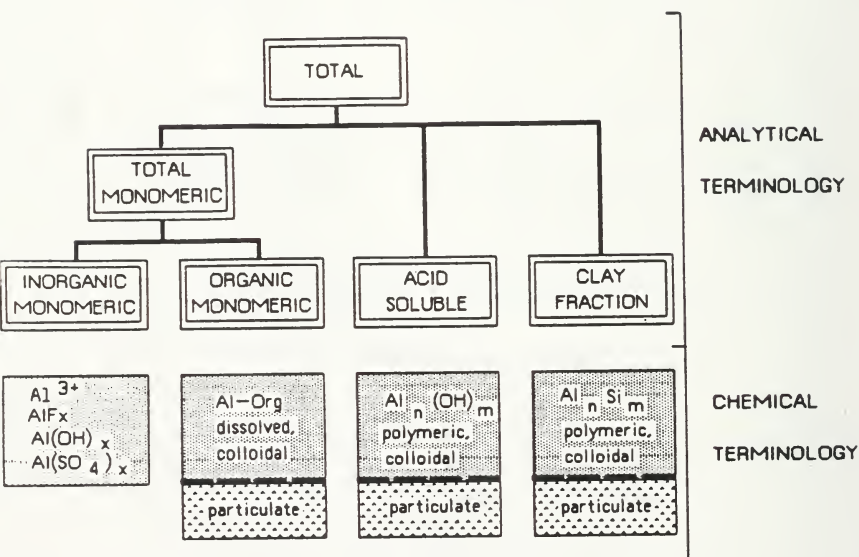
The form of aluminum in water depends on the pH, the presence of other dissolved substances and, to a lesser degree, on the temperature, and period of exposure to the water (Burrows, 1977). The main species of total aluminum measured in a water sample are the inorganic monomeric forms, organic monomeric forms, polymeric complexes, aluminum hydroxide colloids and precipitates, and clays.

2.1 Analytical Methods

A detailed discussion of analytical methods is reserved for the appendix. A summary of that discussion is presented in Fig. 2.1 which attempts to link together known aluminum chemical species with various analytically (operationally) defined subclasses. The choice of analytical terminology is based more on common usage than appropriateness.

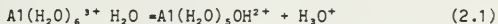
FIGURE 2.1

Aluminum Speciation Terminology at pH < 6.5

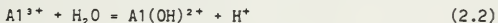


2.2 Inorganic Monomeric Aluminum

When an aluminum salt of a noncomplexing acid such as aluminum chloride is dissolved in pure water, it dissociates to form the hydrated aluminum ion $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Such an aluminum ion is defined as "free" aluminum. In symbol form, the free form of aluminum may be represented as Al^{3+} or $\text{Al}(\text{H}_2\text{O})_6^{3+}$. The latter symbol is more correct because it signifies that Al^{3+} is present in water in association with six (6) water molecules. These two symbols will produce differences in the way the hydration reaction is represented. For $\text{Al}(\text{H}_2\text{O})_6^{3+}$, one can use the reaction:



Whereas for Al^{3+} , one would use the reaction:



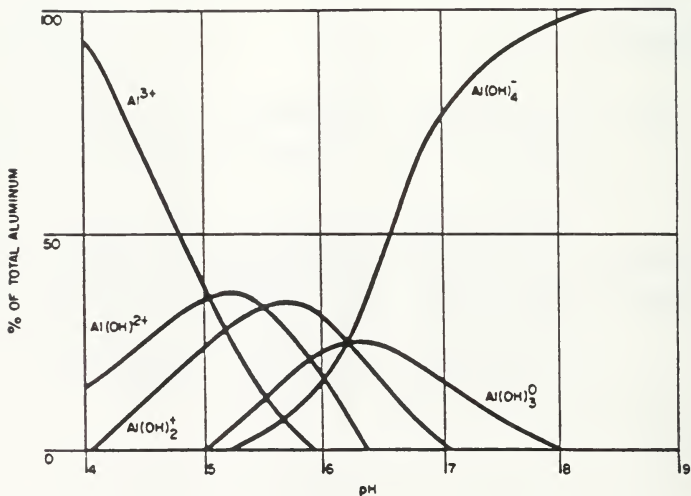
Formulation of the complexation constants for the two reactions show that they are equivalent. In the remainder of this report, the shorter notation Al^{3+} is used.

Free aluminum occurs only in trace amounts in near neutral natural waters due to the domination of hydrolyzed forms of aluminum at pH 7 (Fig. 2.2).

Progressive hydrolysis of the aluminum ion acidifies the solution (eqn 2.2) and leads from the trivalent cation, Al^{3+} , to the hydrolyzed forms. In basic solutions, aluminum exhibits its amphoteric nature by conversion to the aluminum anion, $\text{Al}(\text{OH})_4^-$ (Fig. 2.2).

FIGURE 2.2

Distribution of Soluble Aluminum Hydroxide Species (Adapted from Dyrssen, 1984)



Over the pH range of 4.0 to 5.0 (Figure 2.2), the relative importance of Al^{3+} decreases from 92 to 38% while the proportion of $\text{Al}(\text{OH})^{2+}$ increases from 15 to 36%, and that of $\text{Al}(\text{OH})_2^+$ increases from 0 to 20% (Dyrssen, 1984). The aluminum species distribution illustrated in Figure 2.2 is based upon the existence of $\text{Al}(\text{OH})_3^0$. Its existence has been hypothesized (Baes and Mesmer, 1976), but others (e.g. May et al., 1979) have not confirmed it analytically.

In the vast majority of natural waters of neutral pH, the concentration of aluminum is controlled by the solubility of aluminum hydroxide. The solubility of $\text{Al}(\text{OH})_3(\text{s})$ is controlled by pH, and is minimal in the pH range 5.8 to 7.2 (Figure 2.3). Solubility increases towards both extremes of the pH scale outside the lower solubility range of pH 5.8 to 7.2.

Aluminum is capable of forming strong chemical bonds with substances other than water and hydroxide. In most waters, fluoride and sulphate anions will compete with hydroxide for aluminum (Table 2.1). The presence of these competing ligands may increase the amount of dissolved aluminum in equilibrium with $\text{Al}(\text{OH})_3(\text{s})$. The concentration of dissolved aluminum increases significantly only when sulphate concentrations are greater than 64 mg/L, whereas fluoride levels of only 0.0002 mg/L are required to produce a similar increase in solubility (Hem, 1968). Usually, sufficient fluoride is available such that the aluminum-fluoride (Al-F) complexes dominate the inorganic monomeric aluminum fraction in moderately acidic waters ($5.0 \leq \text{pH} \leq 5.5$; LaZerte 1984).

Conversely, aqueous fluoride chemistry is largely regulated by aluminum concentrations and pH levels in natural waters. At pH values between 5.0 and 5.5, almost all of the soluble fluoride is complexed with aluminum (Hem, 1968). Under higher pH conditions ($\text{pH} > 5.5$), fluoride ligands are unable to compete with hydroxide

FIGURE 2.3

Total Soluble Aluminum as a Function of pH from the Solution of Amorphous $\text{Al}(\text{OH})_3$ (Adapted from Harvey *et al.*, 1981)

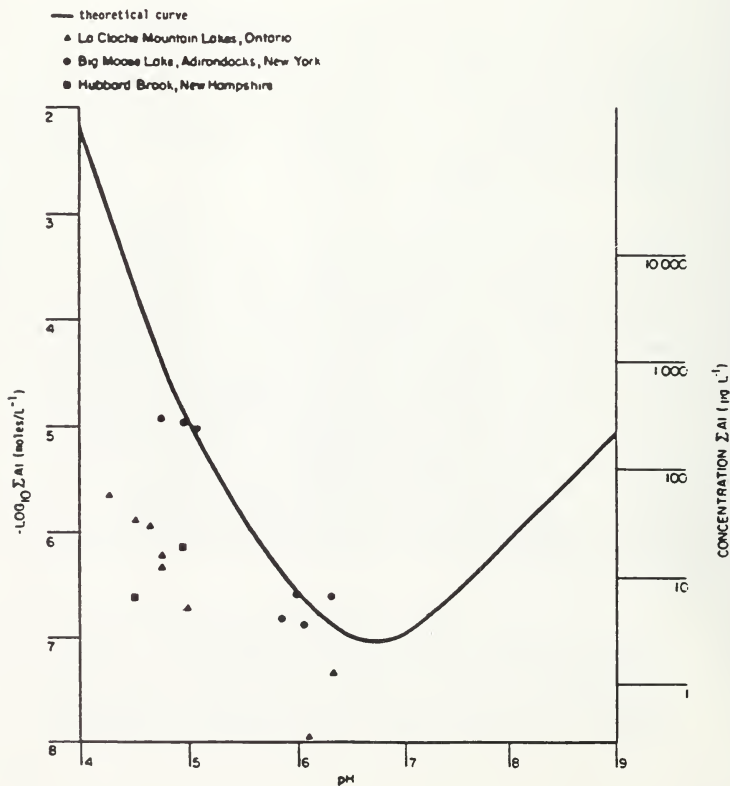
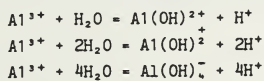
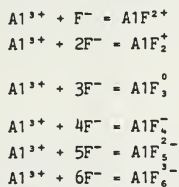


TABLE 2.1 EQUILIBRIUM RELATIONSHIPS OF COMPLEXING LIGANDS

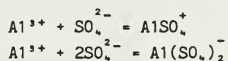
Hydroxide Ligands



Fluoride Ligands



Sulphate Ligands



ligands for aluminum. Consequently, the portion of fluoride which is free increases and the concentration of $Al-F$ complexes decreases. At pH's below 5.0, Al^{3+} begins to dominate the inorganic monomeric aluminum fraction, and free fluoride is again prevalent until HF begins to dominate at very low pH's.

In summary, the speciation of inorganic monomeric aluminum is controlled primarily by pH. The relative concentrations of the major forms are dependent upon the availability of hydroxide and fluoride ligands. Therefore, the measurement of fluoride levels allows the estimation of $Al-F$ species; the remaining aluminum in the inorganic monomeric form can be assumed to be present as Al^{3+} and hydrolyzed forms.

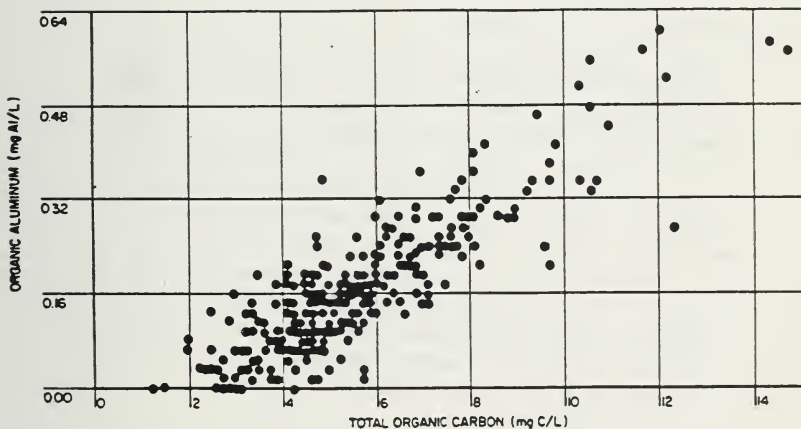
2.3 Organic Monomeric Aluminum

Aluminum can form strong complexes with dissolved organic matter such as fulvic and humic acids to produce organic monomeric aluminum. A correlation determined by Driscoll (1984) for New Hampshire streams and lakes (Figure 2.4) demonstrates the importance of organic carbon levels upon the concentration of organic monomeric aluminum.

High dissolved organic carbon (DOC) levels reduce the concentration of the more toxic inorganic monomeric aluminum, when that aluminum binds with the organic material. As more aluminum complexes with the organic material, the total dissolved aluminum concentration increases. This is one of the most significant factors for explaining discrepancies in total aluminum/toxicity correlations because organic monomeric aluminum complexes are quite stable and do not easily release bound aluminum. Use of total aluminum concentrations confounds the interpretation of toxicity data where DOC concentrations are high. The amount of aluminum complexed varies with the types of organic acids present and increases as the concentration of hydrogen ions decreases. At least 0.025 mg aluminum/mg C can be complexed at pH 4.5 (Neville, 1985), and, in the absence of any other metals, as much as 0.270 mg aluminum/mg C could be complexed at pH 5.5-6.5 (Oliver et al., 1983).

FIGURE 2.4

Organic Monomeric Aluminum Levels in Adirondack Surface Waters as a Function of Solution Total Organic Carbon (TOC) Concentration (Driscoll *et al.*, 1982)



2.4 Polymeric complexes

There is a strong tendency for dissolved aluminum to form polymeric species. When there are three or more hydroxide ligands for every Al^{3+} , the tendency to form polymeric species is enhanced (Smith and Hem 1972). Many polymeric forms are unstable and convert to a solid precipitate upon aging. The increasing size of polymeric forms in unstable solutions is often associated with decreased concentrations of monomeric Al and decreased pH. Some polymeric solutions are, however, quite stable. $Al_3(OH)_4^{3+}$, for example, may be important even at low Al concentrations around pH 6 (Baes and Mesmer 1976).

2.5 Buffering Capacity of Aluminum

An important aspect of aluminum chemistry in acidic surface waters is its role as a pH buffer. Dilute water systems are characteristically low in dissolved inorganic carbon, and are thus limited with respect to inorganic carbon buffering capacity. Dickson (1978) reported that elevated concentrations of aluminum increased the base neutralizing capacity (BNC) of Swedish lakes; Yan and Dillon (1984) reported a similar effect in Sudbury, Ontario lakes. The BNC refers to the equivalent sum of all acids that can be titrated with a strong base. Aluminum BNC can be comparable in magnitude to hydrogen ion and inorganic carbon BNC; therefore, the presence of aluminum increases base dose requirements and the amount of lime required for lake neutralization projects.

2.6 Summary

The species distribution of aluminum is controlled primarily by pH and secondarily by fluoride and organic ligands. As pH and these ligands vary from one body of water to another (even in the same watershed), aluminum species distributions will also differ. The characterization and estimation of aluminum toxicity in aquatic environments will, therefore, be dependent on the availability of species identification and quantification to permit the development of reliable relationships.

3.0 ENVIRONMENTAL DISTRIBUTION

3.1 Aluminum Mobilization

Northern forested ecosystems are generally sensitive to atmospheric deposition of mineral acids when soils are:

- o highly permeable,
- o underlain by silicate bedrock,
- o shallow, and
- o acidic (low in exchangeable base cations:
 $\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+$).

Cronan and Schofield (1979) suggested that mineral acids from atmospheric deposition have altered the natural processes of soil development by facilitating the transport of aluminum from soil to surface waters. The extent of aluminum leaching will depend upon:

- o seasonal variation in the atmospheric deposition of mineral acids to the soil;
- o the rates of organic acid release to the soil from decomposition processes;
- o the neutralization kinetics and acid-buffering capacity of the vegetation and soil; and
- o the size of the watershed drainage area.

3.2 Aluminum Concentrations in Surface Waters

In Ontario, Harvey and Lee (1980) reported that 70% of the La Cloche Mountain lakes sampled had total aluminum concentrations above 0.1 mg/L (range of 0.04 to 0.74 mg Al/L). In a Norway study of 700 lakes, total aluminum concentrations were in the range of 0.05 to 0.30 mg/L in 90% of the lakes (Wright and Snekvik, 1978). The status of fish populations in those lakes was positively correlated with pH and log calcium concentrations, but not with total aluminum. Aluminum concentrations in various southeastern U.S. rivers which contained a large organic content ranged from 0.03 to 0.60 mg/L (Cowgill, 1973).

As discussed in Section 2.0, inorganic aluminum solubility is primarily controlled by pH. The relationship between pH and aluminum levels in Ontario lakes (pH 4.5 to 9.0 is illustrated in Figure 4.1. The relationship between aluminum concentration and pH also tends to be logarithmic in waters of the Adirondacks, Norway and Sweden (Wright et al., 1980) and Quebec (Campbell et al., 1984). Total aluminum concentrations measured in acidic waters ranged from 0.01 to 1.40 mg/L (pH 7.0 to 4.3) in New York State (Schofield, 1976; 0.01 to 0.76 mg/L (pH 7.0 to 4.1) in Sweden (Dickson, 1975; Wenblad and Johansson, 1981); and 0.02 to 0.60 mg/L (pH 7.0 to 4.1) in Norway (Wright et al., 1980). It appears that elevated levels of aluminum are commonly found in acidic waters, and therefore, the opportunity for biotic exposure to aluminum will be much greater in an acidic aquatic environment.

3.3 Aluminum "Bioaccumulation"

Except where gill aluminum concentrations are higher than those in other tissues there is stronger evidence for bioaccumulation of aluminum from the sediments or food than for bioconcentration from the water column. There is no evidence of biomagnification, nor of very high bioconcentration values similar to those for some of the heavy metals, e.g. mercury (at least 17,000) and cadmium (up to 12,400) (M.O.E. 1984). See Appendix II for data, references, and discussion of problems in calculating and interpreting bioaccumulation data based on bioconcentration estimates.

4.0 ALUMINUM TOXICITY

4.1 Factors Affecting Aluminum Toxicity

4.1.1 pH

In the earlier review of aluminum chemistry (Sections 2.2 and 2.3) various species and complexes of aluminum were identified. The presence and predominance of the various species varies with pH, as shown in Fig 2.1 for the aluminum hydroxide species, as well as with the nature of the complexing ligands. Since the toxicity of aluminum varies between different species and complexes (Baker and Schofield, 1982; Driscoll *et al.*, 1980; Schofield and Trojan, 1980; Van Coillie *et al.*, 1983; Skogheim *et al.*, 1984; Neville, 1985) it is apparent that pH has an indirect affect on aluminum toxicity. The hydrogen ion itself is also toxic to aquatic organisms, especially at pH <4.5, but generally, in the pH range covered by these guidelines, hydrogen ion toxicity is minimal compared to that of aluminum.

4.1.2 Dissolved organic carbon (DOC)

A feature of natural waters that greatly modifies the toxicity of aluminum is the presence of organic acids, particularly humic acids which give the characteristic yellowish-brown colour to many lakes and streams. For example, in laboratory experiments when aluminum was added to highly coloured stream water (dissolved organic carbon (DOC)=10 mg/L) to produce a total aluminum concentration of 0.330 mg/L (inorganic aluminum =0.090 mg/L, organic aluminum =0.240 mg/L) at pH 4.5, the medium caused 33% mortality in juvenile rainbow trout during 6 d exposure. Using soft water at the same pH value and calcium concentration, without organic acids, the same level of mortality was caused by only 0.070 mg/L aluminum. Without aluminum at pH 4.5 no

mortality occurred (Neville, 1985). Van Coillie et al. (1983) demonstrated the reduced toxicity of aluminum in the presence of 10 mg/L of sodium humate when the seven-day LC₅₀ for Atlantic salmon was increased from 0.100 mg Al/L at pH 4.65 without Na humate to slightly less than 0.650 mg Al/L at pH 4.54 with Na humate.

4.1.3 Calcium

Although calcium is not important in complexation with aluminum species, ambient calcium concentrations are recognized as playing an important role in gill ion permeability of acid-stressed fish (Packer and Dunson, 1970; McWilliams and Potts, 1978a; McDonald et al. 1983). At calcium levels of 20 mg/L or less, sodium efflux rates are increased. When calcium is absent, acid-exposed fish can lose about 2% of their body sodium per hour (McWilliams, 1982). Losses of chloride would accompany sodium ion losses. Similar effects are seen in fish exposed to acid and aluminum. Increasing calcium concentrations from 0.8 mg/L to 4.2 mg/L has been identified as important in reducing the rate of plasma chloride loss in brown trout (Muniz and Leivestad, 1980). Survival of brown trout exposed to aluminum concentrations up to 0.500 mg/L under pH 5.4 to 4.5 conditions is improved from two to nine-fold when calcium is present at 1 to 2 mg/L compared to survival in 0.5 mg Ca/L exposure solutions (Brown, 1983). Increasing calcium levels from 0.5 mg/L to 8 mg/L in aluminum exposures (0-1.0 mg/L) of brook trout under pH 4.4 to 6.5 conditions also improves survival three to five-fold (Ingersoll et al., 1985). Calcium levels in the fish toxicity studies reported below range from approximately 2-4 mg/L under pH 4.5-6.5 conditions. These values are relevant to Ontario waters (see Fig. 4.3).

4.2 Limitations of criteria based on total aluminum concentrations.

Until recently most studies of aluminum toxicity in aqueous environments have been based on total aluminum concentrations, sometimes measured on filtered (0.45 μm) water samples to avoid the inclusion of aluminum precipitates. These samples may still include suspended and dissolved inorganic and organic forms of aluminum, the proportions of each depending primarily on the aluminum concentration, the pH, and the concentration of organic acids in the water. However, since complexation with organic acids to form organic species reduces aluminum toxicity (see above), toxicity data based on total aluminum levels are misleading and objectives based on total aluminum concentrations should only be applied to water with very low dissolved organic carbon (DOC) levels.

The concentrations of total aluminum measured in unfiltered samples from 1,881 Ontario inland lakes with pH values ranging from 4.5-9.0 are shown in Fig. 4.1. DOC and Ca^{2+} concentrations in the same lakes are shown in Figs. 4.2 and 4.3 respectively. Since 1 mg/L DOC can complex approximately 0.025 mg/L aluminum at pH 4.5, and the complexing capacity increases as pH increases (see Section 2.3), it can be seen that almost all of the total aluminum could be complexed with organic acids in the majority of the lakes with pH values >6.0 . Even at pH 5.0-6.0 most of the aluminum could be organically complexed, especially if iron concentrations are low. However, in many of the lakes at pH 4.5-5.0 the total aluminum could be mostly inorganic.

In rivers and streams the modifying effect of humic acids (DOC) on aluminum toxicity may be reduced. Reported DOC concentrations for Ontario rivers and streams range from 1.0 to 22.5 mg/L but many more of the available sites for complexation on the DOC molecules may be taken up by competing substances in contaminated water samples from industrial, agricultural, and urban areas. Also, much of the aluminum may be complexed with other ligands.

FIGURE 4.1 Total aluminum concentrations (mean \pm s.d.) in Ontario inland lakes at pH 4.5 - 9.0 (MOE, MNR extensive lakes data base).

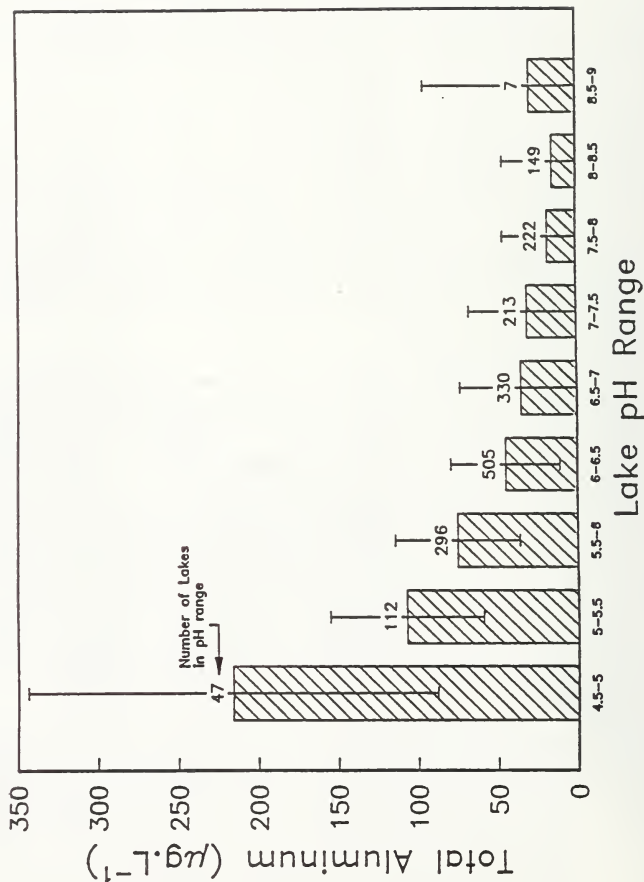


FIGURE 4.2 Dissolved organic carbon concentrations (mean \pm s.d.) in Ontario inland lakes at pH 4.5 - 9.0 (MOE, MNR extensive lakes data base).

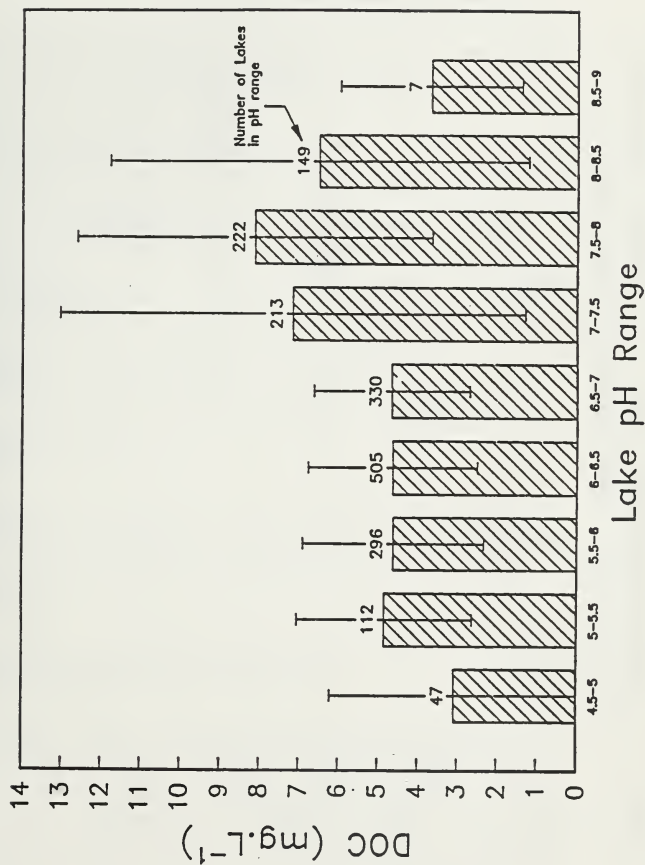
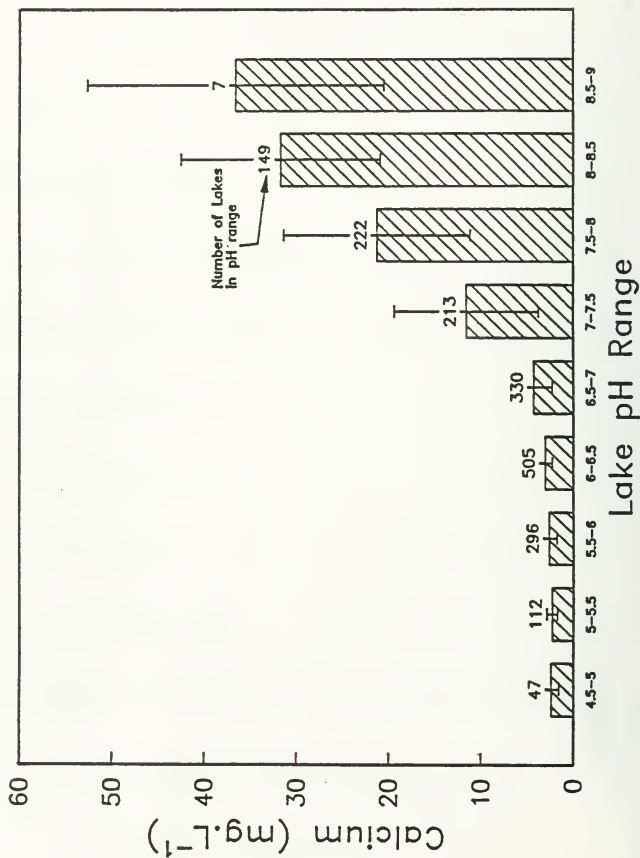


FIGURE 4.3 Calcium concentrations (mean \pm s.d.) in Ontario inland lakes at pH 4.5 - 9.0 (MOE, MNR extensive lakes data base).



Prediction of the possible toxicity of total aluminum concentrations is therefore even more difficult with samples from rivers and streams than from inland lakes. This is especially so with concentrations measured in unfiltered samples. The occurrence of high concentrations of suspended solids including clay particles is much greater in the river and stream samples, especially in times of heavy runoff, and much of the aluminum in such turbid waters is probably not bioavailable. Data have been collected from approximately 150 monitoring stations in Ontario, including stations downstream of municipal and industrial point sources, and urban, agricultural and background stations. Total aluminum concentrations (mean, median and range) of 1,886 observations in the pH range 6.5 - 9.0 were 0.669 mg/L, 0.150 mg/L and 0.001 - 41.0 mg/L respectively. However, observations on 157 samples from a limited number of stations, primarily in southern Ontario, that would reflect values as close as possible to background levels showed total aluminum concentrations of 0.068 mg/L (mean), 0.040 mg/L (median), and ranged from 0.001-0.470 mg/L (Ontario Ministry of the Environment, River Systems Section).

Without the inclusion of clay particles many of these observations may be much lower. Nevertheless, these data show that there is considerable aluminum input from anthropological sources.

4.3 Rationale for the use of inorganic and total forms of aluminum in criteria for the pH range 4.5-9.0.

Inorganic forms of aluminum have been shown to increase the toxicity of aqueous environments at pH 4.5-6.5 but there is a paucity of inorganic aluminum data at pH levels >6.5. Therefore, to optimize the validity and range of applications at pH 4.5-6.5 criteria based on inorganic aluminum concentrations will be developed. However, at present the criterion for pH values >6.5-9.0 will have to be based on total aluminum concentrations (see Section 4.5). In both cases any clay fractions are excluded (see Appendix I for analytical procedures).

4.4 Inorganic Aluminum Toxicity at pH 4.5-6.5.

4.4.1 Toxic forms of inorganic aluminum.

Inorganic monomeric aluminum (IMAL) (Fig. 2.1), is the toxic form of dissolved inorganic aluminum (Driscoll et al., 1980). It is the major inorganic form of aluminum present at low aluminum concentrations in the pH range 4.5 to approximately 5.4, but there is a substantial amount of evidence (see Fig. 4.4 to 4.8) that at intermediate pH values toxicity may be caused by part of the acid soluble inorganic aluminum shown in Fig. 2.1, instead of or as well as IMAL. Except in the case of benthic organisms only the acid soluble fraction remaining in the water column would be involved. Data used for the development of the objectives are from studies in which the inorganic aluminum in the water column and/or IMAL concentrations were reported, or from studies where it could be assumed that in the experimental protocol used the DOC levels were low enough such that organic aluminum did not constitute a significant amount of the total aluminum measured. It is assumed that in all studies any clay fractions were insignificant. Depending on the pH and solubility level, the inorganic aluminum may have all been monomeric or may have been a mixture of monomeric and suspended acid soluble aluminum as defined in Fig. 2.1. Where IMAL concentrations were measured they are shown in the text.

4.4.2 Species Excluded Due To Lack of Suitable Data.

The data which fulfill the requisites for inorganic aluminum guidelines in acidic environments in Ontario are almost exclusively from studies on fish. Inorganic aluminum concentrations could not be calculated from studies reporting total aluminum toxicity to bacteria and macrophytes because exposures included aluminum in the sediments. Similarly, most algal and invertebrate studies also had to be eliminated because lake or stream

water was used; therefore unknown amounts of organic aluminum were present. Helliwell et al. (1983) reported concentrations of inorganic aluminum species that could not be used because calcium concentrations in the exposure medium were far higher than normally found in the pH 4.5-6.5 range. Amphibian data were not included because studies were primarily at pH levels <4.5, where acid toxicity is usually greater than aluminum toxicity to other classes of organisms.

4.4.3 Invertebrates

Data are available from one study on invertebrates. Daphnids (Daphnia magna) were exposed for 24 h to varying concentrations of acid and inorganic aluminum at different calcium concentrations in artificial soft water. Aluminum was more toxic than the acid at pH 5.5. Addition of 0.054 mg/L inorganic aluminum increased mortality by approximately 10% with calcium concentrations of 4 and 20 mg/L and by 50-60% with very low calcium concentrations of 0.4 and 0.04 mg/L (M. Havas, pers. comm.).

4.4.4 Fish

The data for lethal and sublethal effects of aluminum on fish at pH 4.5-6.5 with Ca^{2+} = 2.0 to 4.0 mg/L are shown in parts 4.4.4.1 to 4.4.4.4 and in Figs. 4.4 to 4.7. The figures include approximate solubility lines for $\text{Al}(\text{OH})_3$ (Harvey et al., 1981), and show that at pH >5.2 almost all of the data relate to supersaturated conditions for inorganic aluminum. Only the data which show acid and aluminum effects greater than acid only effects are included. Where a wide range of aluminum and/or pH values are reported only the minimum aluminum and maximum and minimum pH values are included; with a small range of values only the means are shown. Sac fry and swim-up fry data are combined.

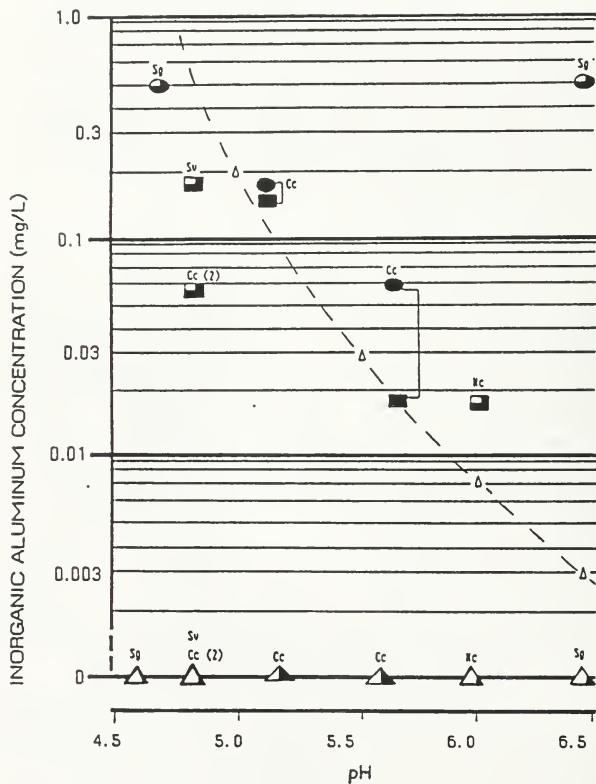


FIGURE 4.4

Lethal Toxicity of Inorganic Aluminum to Fish Eggs at Specific pH Conditions from 4.5 - 6.5

(FIGURE 4.4 Contd.)

LEGEND

GEOMETRIC SHAPES

- = Total inorganic aluminum
- = Monomeric inorganic aluminum
- Total & monomeric inorganic aluminum within same sample
- △ = Control (no aluminum)

APPROXIMATE LEVEL OF MORTALITY

- = 100%
- = 75%
- = 50%
- = 25%
- = 0%

SOLUBILITY CURVE

- △---△ = Solubility of $Al(OH)_3$
- (From Harvey et al., 1981.)

SPECIES

Symbol	Scientific Name	Common Name	Reference
Cc	<u>Catostomus commersoni</u>	White sucker	Baker & Schofield, 1982
Cc(2)	" "	" "	Holtze et al. In prep.
Nc	<u>Notropis cornutus</u>	Common shiner	" " " "
Sg	<u>Salmo gairdneri</u>	Rainbow trout	Holtze, 1983
Sv	<u>Stizostedion vitreum</u>	Walleye	Holtze et al. In prep.

(FIGURE 4.5 Contd.)

LEGEND

GEOMETRIC SHAPES	APPROXIMATE LEVEL OF MORTALITY	SOLUBILITY CURVE
○ = Total inorganic aluminum	● ■ = 100%	Δ --- Δ = Solubility of $Al(OH)_3$
□ = Monomeric inorganic aluminum	◐ ◑ = 75%	(From Harvey <i>et al.</i> , 1981.)
◌ Total & monomeric inorganic aluminum within same sample	◒ ◓ ▲ = 50%	
	◔ ◕ ◖ ◗ = 25%	
△ = Control (no aluminum)	○ □ △ = 0%	

SPECIES

Symbol	Scientific Name	Common Name	Reference
Cc	<u>Catostomus commersoni</u>	White sucker	Baker & Schofield, 1982
Cc(2)	" "	" "	Holtze <i>et al.</i> In prep.
Sf	<u>Salvelinus fontinalis</u>	Brook Trout	Baker & Schofield, 1982
Sg	<u>Salmo gairdneri</u>	Rainbow Trout	Holtze, 1983
Sn	<u>Salvelinus namaycush</u>	Lake Trout	Gunn & Keller, 1984
Sv	<u>Stizostedion vitreum</u>	Walleye	Holtze <i>et al.</i> In prep.

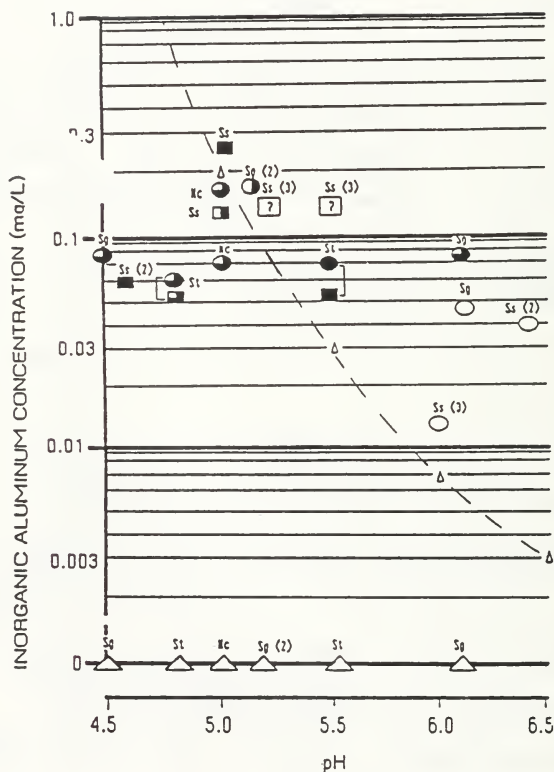


FIGURE 4.6

Lethal Toxicity of Inorganic Aluminum to Fish Fingerlings, Juveniles, and Adults at Specific pH Conditions from 4.5 - 6.5

(FIGURE 4.6 Contd.)

LEGEND

GEOMETRIC SHAPES

- = Total inorganic aluminum
- = Monomeric inorganic aluminum
- □ = Total & monomeric inorganic aluminum within same sample
- △ = Control (no aluminum)

APPROXIMATE LEVEL OF MORTALITY

- ■ = 100%
- ◐ ◑ = 75%
- ◒ ◓ △ = 50%
- ◔ ◕ ◖ ◗ = 25%
- ◘ ◙ ◚ ◛ = 0%
- ◜ ◝ = Field study. % mortality unknown

SOLUBILITY CURVE

△ --- △ = Solubility of $Al(OH)_3$

(From Harvey et al., 1981.)

SPECIES

Symbol	Scientific Name	Common Name	Reference
Nc	<u>Notropis cornutus</u>	Common shiner	Kramer et al., 1986
Sg	<u>Salmo gairdneri</u>	Rainbow trout	Neville, 1985
Sg(2)	" "	" "	Orr et al., 1986
Ss	<u>Salmo salar</u>	Atlantic salmon	Rosseland & Skogheim, 1982
Ss(2)	" "	" "	" " 1984
Ss(3)	" "	" "	Skogheim et al., 1984
St	<u>Salmo trutta</u>	Brown trout	Sadler & Lynam, 1986

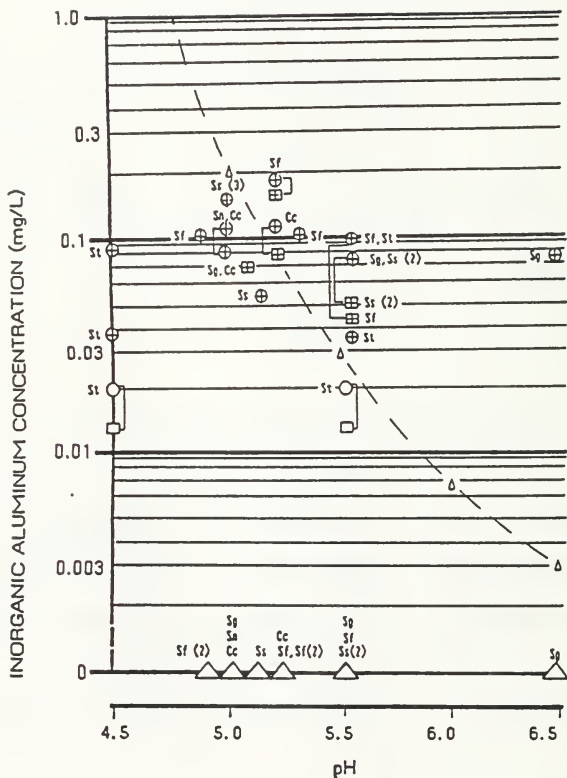


FIGURE 4.7

Sublethal Toxicity of Inorganic Aluminum to Various Life Stages of Fish at Specific pH Conditions from 4.5 - 6.5

(FIGURE 4.7 Contd.)

LEGEND

GEOMETRIC SHAPES

○ = Total inorganic aluminum

□ = Monomeric inorganic aluminum

○ □ = Total & monomeric inorganic aluminum within same sample

△ = Control (no aluminum)

LEVEL OF EFFECTS

⊕ ⊞ = Significant adverse effects

○ □ △ = No adverse effects

SOLUBILITY CURVE

△---△ = Solubility of $Al(OH)_3$

(From Harvey *et al.*, 1981.)

SPECIES

Symbol	Scientific Name	Common Name	Reference
Cc	<u>Catostomus commersoni</u>	White sucker	Baker & Schofield, 1982
Sf	<u>Salvelinus fontinalis</u>	Brook trout	" " "
Sf(2)	" "	" "	Schofield & Trojnar, 1980
Sg	<u>Salmo gairdneri</u>	Rainbow trout	Neville, 1985
Sn	<u>Salvelinus namaycush</u>	Lake trout	Gunn, 1987
Ss	<u>Salmo salar</u>	Atlantic salmon	Henriksen <i>et al.</i> , 1984
Ss(2)	" "	" "	Jagoe <i>et al.</i> , 1987
Ss(3)	" "	" "	Rosseland & Skogheim, 1982
St	<u>Salmo trutta</u>	Brown trout	Sadler & Lynam, 1986

4.4.4.1 Eggs

The sensitivity of eggs to inorganic aluminum in the pH range 4.5-6.5 varies considerably among species. Baker and Schofield (1982) carried out a series of experiments with inorganic aluminum concentrations near to the saturation point at the various pH levels (see Fig. 4.4). The inorganic aluminum had no effect on the hatching of brook trout (Salvelinus fontinalis) eggs (0-10% mortality) exposed for 2 months to concentrations from 0.050 mg/L at pH 5.5 to 0.100-0.500 mg/L at pH 4.6. White sucker (Catostomus commersoni) eggs exposed for 3 weeks were much more sensitive to acid and to acid + aluminum than brook trout eggs. Mortality was 100% with or without 0.190-0.480 mg Al_{inorg}/L (IMAL = 0.170-0.470) at pH 4.6-4.8. However inorganic aluminum increased toxicity at pH 5.2-5.6. Exposure to the acid alone caused up to 60% mortality but with 0.150 mg Al_{inorg}/L (IMAL = 0.130) at pH 5.2 and 0.060 mg/L (IMAL = 0.020) at pH 5.6, mortality was 100%.

Holtze et al. (in prep.) also found eggs of non-salmonid species to be sensitive to inorganic aluminum. Mortality increased by 20-40% during fertilization to hatch in white sucker and walleye (Stizostedion vitreum) eggs exposed to 0.058 (IMAL) and 0.172 (IMAL) mg/L respectively at pH 4.8, and in common shiner (Notropis cornutus) eggs exposed to 0.018 (IMAL) mg/L at pH 6.0, compared to controls at the same pH values without aluminum.

Rainbow trout (Salmo gairdneri) eyed eggs experienced mortality levels of 15-30% in the recovery period following 8 d exposure with and without 0.100 mg Al_{inorg}/L at pH 4.6-6.5. However, with 0.500 mg/L mortality increased to 35-85% (Holtze, 1983).

Despite the relative insensitivity of salmonid eggs, the lowest levels of inorganic aluminum and IMAL shown in these data to cause mortality to fish eggs at pH 4.5-6.5 are 0.060 mg/L and 0.018 mg/L respectively.

4.4.4.2 Fry

In acid waters with inorganic aluminum concentrations close to the saturation point brook trout fry are slightly more sensitive than eggs, and the swim-up stage is more sensitive than the sac fry stage. After 2 weeks exposure at pH 4.6 mortality was less than 10% without aluminum but with 0.500 mg Al_{inorg}/L it increased to 30-50% in sac fry and 80-85% in swim up fry. At pH 4.9 mortality was < 5% with 0-0.300 mg/L in sac fry, and 0-0.100 mg/L in swim up fry, but in the latter mortality was 60% with 0.300 mg/L (IMAL = 0.270). At pH 5.2-5.5, moderately supersaturated inorganic aluminum concentrations (0.170 mg/L (IMAL = 0.150) at pH 5.2 and 0.070 mg/L (IMAL = 0.050) at 5.5) caused mortality in 20% of sac fry and 40% of swim up fry at pH 5.2 but had no effect at pH 5.5. Grossly supersaturated solutions (0.400 mg/L (IMAL = 0.260) at pH 5.2 and 0.170 mg/L (IMAL = 0.060) at pH 5.5 caused 50-100% mortality in both life stages (Baker and Schofield, 1982).

White sucker fry were more sensitive than brook trout fry. In sac fry, 100% mortality occurred during 2 weeks exposure to pH 4.6-4.8 with and without 0.090-0.470 mg Al_{inorg}/L (IMAL = 0.090-0.450). However, at pH 5.0 mortality increased from 45-60% without aluminum to 80-100% with 0.085 and 0.260 mg/L (IMAL = 0.085-0.235), and at pH 5.2-5.4 it increased from <5% in the controls to 100% with 0.170 mg/L (IMAL = 0.120) at pH 5.2 and 0.050 mg/L (IMAL = 0.050) at pH 5.4. In swim up fry at pH 4.8-5.6 control mortalities were 0-20% but increased to 60-100% with 0.190 mg Al_{inorg}/L (IMAL = 0.160) at pH 4.8, 0.090 mg/L (IMAL = 0.075) at pH 5.0, and 0.120 mg/L (IMAL = 0.080) at pH 5.2 and to 35% with 0.090 mg/L (IMAL = 0.050) at pH 5.6 (Baker and Schofield, 1982).

Rainbow trout fry are less sensitive to acid than white sucker fry in the sac fry stage but are equally sensitive to acid + aluminum. Mortality of sac fry and swim-up fry at pH 4.5 was less than 5% during 8 d exposure without aluminum, but rose to 90-100% with 0.100 mg AL_{inorg}/L (Holtze, 1983).

Exposure from the cleavage egg stage to 4 d post hatch at pH 4.8 with 0.058 mg/L IMAL (white suckers) or 0.030 mg/L IMAL (walleye) caused over 90% mortality compared to 35% (white suckers) and 55% (walleye) mortality at pH 4.8 without aluminum (Hutchinson and Holtze, 1985). In field studies, using lower inorganic aluminum concentrations, Gunn & Keller (1984) found that mortality of lake trout (Salvelinus namaycush) sac fry rose from approximately 5% during 5 d exposure to 0.010 mg/L IMAL at pH 4.5-5.5, to 18% with 0.050 mg/L IMAL.

From these data, the lowest levels of inorganic aluminum and IMAL shown to cause mortality of fish sac fry and swim up fry at pH 4.5-6.5 are 0.050 mg/L and 0.030 mg/L respectively.

4.4.4.3 Fingerlings, Juveniles, and Adults

The sensitivity of older life stages of fish is often similar to fry and greater than that of eggs. Sadler and Lynam (1986) found that during 6 weeks exposure of brown trout (Salmo trutta) fingerlings to inorganic aluminum concentrations of 0.062 mg/L (IMAL = 0.052) at pH 4.8 there was 70% mortality, and 100% mortality occurred in fingerlings exposed to 0.072 mg/L (IMAL = 0.051) at pH 5.5. Mortality at these pH values without aluminum was less than 5%. After only 5 days exposure of fingerling rainbow trout, Orr et al. (1986) found the LC₅₀ at pH 5.1 to 5.3 to be 0.175 mg/L inorganic aluminum.

In Atlantic salmon (Salmo salar) presmolts, mortality was 100% within 50 h of exposure to pH 5.0 with 0.245 mg/L inorganic monomeric aluminum and 40% within 60 h with 0.130 mg/L (eyed eggs at these concentrations were unaffected). Yearling sensitivity was intermediate between that of presmolts and eyed eggs (Rosseland and Skogheim, 1982). 75% mortality occurred in rainbow trout juveniles (200-470 g) exposed for up to 11 d to 0.075 mg Alinorg/L at pH 4.5 and 6.1. There was no mortality in the control groups (pH 4.5 and 6.1 without aluminum) nor at pH 6.1 with 0.045 mg/L (Neville, 1985).

Using adult fish, Kramer et al. (1986) report 50-100% mortality in common shiners within 7 h exposure to 0.070-0.160 mg Alinorg/L at pH 5.0. There was no mortality in the controls at pH 5.0 without aluminum.

In field studies Rosseland and Skogheim (1984) found 100% mortality within 36 h exposure of Atlantic salmon smolts to inorganic monomeric aluminum concentrations of 0.050-0.065 mg/L at pH 4.6. Mortality in the field at this pH without aluminum could not be determined. However, there was no mortality at pH 6.4-6.8 with 0.030-0.040 mg/L. Skogheim and Rosseland (1984) report no mortality in spawning Atlantic salmon at pH 6.0 with 0.013 mg/L inorganic monomeric aluminum but mortality was observed ($n > 50$) within 35 h exposure to pH 5.2-5.5 with 0.109-0.133 mg/L.

The lowest inorganic aluminum and IMAL levels shown by these data to cause mortality of fingerling to adult life stages of fish at pH 4.5-6.5 are 0.062 mg/L and 0.051 mg/L respectively.

4.4.4.4 Sublethal Effects

Reports of sublethal effects have generally been limited to readily observable responses in fish, such as behavioural changes, fry growth, or ventilation changes, all of which are visible indications of physiological stress. These changes have been reported in laboratory and field studies carried out in the pH 4.5-5.5 range.

The cessation of feeding, reduced activity or sluggishness and a darkened pigmentation have been observed in Atlantic salmon presmolts during 6 d exposure in field cages to pH 5.1-5.5 and 0.053-0.077 mg Al_{inorg}/L. Some mortality also occurred. Controls were unaffected (Henriksen et al. 1984).

In laboratory studies, brook trout fry growth was reduced by 20% during 14 d exposure to 0.180 mg Al_{inorg}/L (IMAL = 0.145) at pH 5.2, and by 14% with 0.085 mg Al_{inorg}/L (IMAL = 0.045) at pH 5.5. White sucker appear to be more sensitive than salmonids. After 13 d exposure to 0.090-0.120 mg Al_{inorg}/L (IMAL = 0.080) at pH 5.0 and 5.2, growth was reduced by 50% (Baker and Schofield, 1982). Schofield and Trojnar (1980) found that 0.100 mg Al_{inorg}/L reduced growth of brook trout fry by 20% at pH 4.9, and caused clubbing at the distal ends of gill filaments at pH 5.2, also after 14 d exposure. Brown trout fingerlings exposed to pH values from 4.5 to 5.5 for 6 weeks showed growth reductions of 30-80% with 0.081-0.038 mg Al_{inorg}/L (IMAL = 0.081-0.012), but no growth reduction with 0.031-0.019 mg/L (IMAL = 0.028-0.012) (Sadler and Lynam, 1986). Newly hatched Atlantic salmon exposed to pH 5.5 without aluminum for 60 d showed no difference in gill development or growth from control fish at pH 7.2. However, in the presence of 0.075 mg/L inorganic aluminum (IMAL = 0.045-0.060) at pH 5.5, gill development was impaired by day 30 and total body length was significantly reduced by day 60 (Jagoe et al., 1987). Lake trout sac fry exhibited delayed growth compared to control fish after a 30 d recovery period following 5 d exposure to pH 5.0 + 0.106 mg/L inorganic aluminum. No mortality occurred in either group (Gunn and Noakes, 1987).

Persistent moderately increased ventilation rates and/or amplitude have been observed in juvenile rainbow trout exposed in

respiratory chambers for 6-11 d to 0.075 mg Alinorg/L at pH 5.5 and 5.0. The same concentration caused a slight ventilatory response at pH 6.5. At pH 5.0 the aluminum also caused loss of Na^+ and Cl^- ions from plasma and tissue. Control fish at pH 6.5, 5.5 and 5.0 without aluminum were unaffected. (More severe responses to the aluminum at pH 4.5 and 6.1 led to 75% mortality in 2-8 d), (Neville, 1985). Rosseland and Skogheim (1982) also found respiratory impairment and loss of plasma Na^+ and Cl^- in Atlantic salmon presmolts exposed for 3 d to 0.130 mg Alinorg/L at pH 5.0.

In these studies the lowest inorganic aluminum and IMAL concentrations to cause sublethal effects to fish at pH 4.5-5.5 are both 0.038 mg/L.

For all life stages of fish these data indicate that inorganic aluminum and IMAL concentrations should be less than 0.038 mg/L and 0.030 mg/L respectively at pH 4.5-5.5 and 0.060 mg/L and 0.018 mg/L respectively at pH 5.6-6.5 to avoid sublethal effects or lethality.

4.5 Total Aluminum Toxicity at pH >6.5-9.0.

At pH >6.5-9.0 aluminum toxicity tests have primarily used concentrations >1 mg/L to assess the environmental effect of the aluminum flocculation process used in many water treatment plants. There has been little concern over aluminum toxicity at concentrations <1.0 mg/L, and consequently little toxicity research or analytical procedure development. However, such concentrations have been shown to be toxic. In contrast to the pH 4.5-6.5 range, at pH >6.5-9.0 it is currently not possible to separate organic and inorganic forms of aluminum unless a time consuming dialysis procedure is used, nor has the non-toxic nature of organic aluminum been confirmed. The aluminum objective for pH >6.5-9.0 is therefore based on total aluminum concentrations in samples excluding any clay fraction (see Appendix I for analytical procedure).

Table 4.1 summarizes data using total aluminum concentrations of <1.0 mg/L on various species including a diatom, an alga, a daphnid, an aquatic insect and 5 species of fish. No effect concentrations on fish are also included. Fig. 4.8 shows the lethal, sublethal, and no effect levels reported in the table and includes an approximate solubility line for $Al(OH)_3$, (Harvey et al., 1981).

The toxic aluminum concentrations range from 0.150 to 0.832 mg/L, and include dissolved and suspended (ie. not dissolved but still present in the water column) forms of aluminum, the proportion of each depending on the pH used as shown by the solubility line for $Al(OH)_3$, (Harvey et al., 1981). Freeman and Everhart (1971) have shown both of these forms of aluminum to be toxic to rainbow trout fingerlings in laboratory studies with 0.514 mg/L aluminum at pH 6.6-8.0. As with most of the laboratory studies in the table, aluminum chloride was used in the test solutions. Toxicity levels appear to be similar to those of aluminum sulphate solutions. Tests using lake water as the diluent will probably also include some forms of organic aluminum which may not be toxic. The concentration of these will vary with the pH and the dissolved organic carbon (DOC) content of the water. Suspended aluminum hydroxide may also be present in these tests.

Call et al. (1984) reported one of the problems found in using grossly supersaturated solutions. The nominal concentrations used in their experiments were 0.4, 0.8, 1.6, 3.2 and 6.4 mg/L. However, 6.4 mg/L produced the lowest initial aluminum concentration in the water column (0.3 mg/L), the highest (0.8 mg/L) was produced by 1.6 mg/L.

The lowest toxic concentrations reported are in fish studies. Two laboratory studies and one field study report toxicity at 0.150 to 0.170 mg/L aluminum. No effect concentrations on fish were reported using 0.045-0.060 mg/L aluminum.

Table 4.1: Toxicity of Total Aluminum Concentrations of <1.0 mg/L at pH >6.5-9.0.

#	Species	Al Cono.	pH	Duration	Procedure ¹	Effect	Reference
1.	Diatom <u>Cyclotella meneghiniana</u>	0.810	7.9	8 d	St. U.	Growth inhibition	Rao and Subramanian, 1982
2.	Green alga <u>Selenastrum capricornutum</u>	0.570 ^{***} 0 - 96h	7.6-7.5 0 - 96h	4 d	St. M.	Biomass EC ₅₀	Call et al. 1984
3.	Green Alga <u>Selenastrum capricornutum</u>	0.460 ^{***} 0 - 96h	8.2-7.5 0 - 96h	4 d	St. M.	Biomass EC ₅₀	Call et al. 1984
4.	Cladoceran <u>Daphnia magna</u>	0.320 ^{*,*}	7.7	21 d	St. M.	Reduced reproduction	Biesinger and Christensen, 1972
5.	Midge (larvae) <u>Tanytarsus dissimilis</u>	0.832 ^{*,*,*}	6.8	55 d	St. M.	37% mortality	Lamb and Bailey, 1981
6.	Rainbow trout (eggs) <u>Salmo gairdneri</u>	0.500 [*]	7.2	8 d exposure +12 d recovery	St. M.	56% mortality	Holtze, 1983
7.	Rainbow trout (fingerlings) <u>Salmo gairdneri</u>	0.513	7.3-6.6	44 d	F1. M.	<50% mortality	Freeman and Everhart, 1971
8.	Rainbow trout (fingerlings) <u>Salmo gairdneri</u>	0.514	8.0	44 d	F1. M.	40% weight reduction	Freeman and Everhart, 1971

Table 4.1 Cont'd....

Species	Al Conc.	µl	Duration	Procedure ¹	Effect	Reference
9. Rainbow trout (embryos & fry) <u>Salmo gairdneri</u>	0.560	7.4	28 d	Fl. M	EC ₅₀ (death & deformity)	Birge et al. 1980
10. Rainbow trout (embryos & fry) <u>Salmo gairdneri</u>	0.369	7.4	28 d	Fl. M.	EC ₅₀ (death & deformity)	Birge et al. 1980
11. Goldfish (embryos & fry) <u>Carassius auratus</u>	0.150	7.4	7 d	Fl. M.	EC ₅₀ (death & deformity)	Birge, 1978a
12. Largemouth bass (embryos & fry) <u>Micropterus salmoides</u>	0.170	7.2-7.8	8 d	Fl. M.	50 % mortality	Birge, 1978b
13. Brown trout (yearlings) <u>Salmo trutta</u>	(0.137) ^{a,*,*} -0.150	(6.3)-6.9	10 months	Field M.	Gill deformity, increased opercular movement, skin darkening	Karlsson-Norrgren, 1986
14. Rainbow trout (fingerlings) <u>Salmo gairdneri</u>	0.052	7-9	45 d	Fl. M.	No effect	Freeman and Everhart, 1971
15. Rainbow trout (sac fry) <u>Salmo gairdneri</u>	0.045 ^{*,*}	7.1	-60 d	Field M.	98% survival	Gunn & Keller, 1984b
16. Lake trout <u>Salvelinus namaycush</u> (sac fry)	0.060 ^{*,*}	7.6	-60 d	Field M.	90-94% survival	Gunn & Keller, 1984b

Table A.1 Cont'd....

FOOTNOTE:

- St = static exposure; U = unmeasured concentration; M = measured concentration; F1 = flowthrough exposure; Field = field study.
- Lake water used to make up test solutions
- Aluminum concentrations measured on acidified samples from water column.
- Aluminum concentration added to unfiltered lake water
- 0.45 um filtered lake water
- Aluminum sulphate used in test procedures
- Field study
- Brown trout reared at fish farm supplied by water from a lined "acid lake".
- Unfiltered sample from clear, colourless, lake.

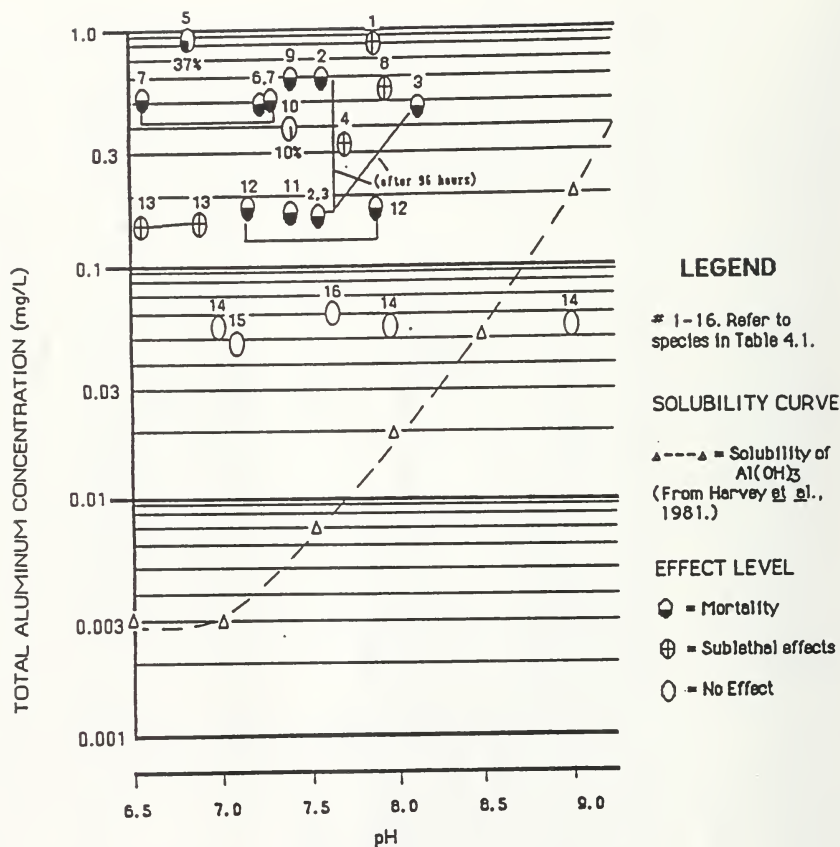


FIGURE 4.8

Total Aluminum Toxicity at Conc. < 1 mg/l and Specific pH Conditions from 6.5 - 9.0

5.0 CRITERIA DEVELOPMENT

A Provincial Water Quality Objective (P.W.Q.O.) or Provincial Water Quality Guideline (P.W.Q.G.) is based upon some fraction of the lowest concentration that effects the most sensitive aquatic organism and life-stage. Previously, P.W.Q.O.'s for metals have been based on total metal concentrations, and have been measured in unfiltered samples. However, more recent research has shown that not all forms in which a metal may exist in the environment are necessarily toxic. If the total metal concentration in a given water body consists primarily of non-toxic forms the criterion concentration could be exceeded without any evidence of a toxic impact. Therefore, whenever possible the criteria should be based on concentrations of toxic forms of the metal.

Aluminum toxicity is strongly influenced by the ambient pH and the presence of various complexing organic and inorganic anions. However, these factors, and the inclusion of clay particles, complicate the laboratory analysis of water samples for identification and quantification of the toxic forms. At present the toxic forms of aluminum have been more closely identified at low pH (4.5 to 5.5) than at mildly acidic pH values (>5.5 to 6.5) and have not yet been specified at pH >6.5 to 9.0. As discussed in the following sections, criteria based on different forms of aluminum have had to be developed for these three pH ranges. Sufficient data to derive specific numerical criteria with assurance were only available for the pH ranges 4.5 to 5.5 and >6.5 to 9.0. Normally these criteria can be used independently of natural background aluminum concentrations, but in some water bodies unaffected by man-made inputs the natural background level may exceed the criterion. In such cases, and in the pH range >5.5 to 6.5, interim recommendations for limiting the discharge of aluminum have been derived based on the natural aluminum concentrations of the appropriate water bodies.

5.1 pH range 4.5-6.5

The aluminum criteria for pH 4.5 to 5.5 and pH >5.5 to 6.5 are developed from the data discussed in Sections 4.4.4.1 to 4.4.4.4, shown in detail in Figs. 4.4 to 4.7, and summarized in Fig. 5.1. Figures 4.4 to 4.7 show that the lowest measured concentrations of inorganic aluminum producing lethal and sub-lethal effects are relatively constant (0.030 to 0.100 mg/L) across the pH range 4.5 to 6.5. They do not show any marked consistent trend with pH but the predominant form of inorganic aluminum at these concentrations may change from monomeric to polymeric or larger forms at approximately pH 5.5. Physiological evidence shows that the predominant mechanism of toxicity also changes from impaired ionoregulation to impaired oxygen uptake at approximately pH 5.5 (Neville, 1985). Therefore, the criteria are based on inorganic monomeric aluminum for pH 4.5 to 5.5, and acid soluble inorganic aluminum for pH >5.5 to 6.5.

5.1.1 pH 4.5-5.5

Table 5.1 shows the highest no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC) in data from the species and life stages discussed in Sections 4.4.4.1 to 4.4.4.4. Of these, the lowest LOEC for inorganic monomeric aluminum in the pH range 4.5 to 5.5 is for fry (walleye sac fry development, LOEC = 0.030 mg/L at pH 4.8) showing this to be the most sensitive life stage. The highest NOEC for the same life stage and pH range is 0.010 g/L (lake trout survival). Aluminum does not cause organoleptic effects, nor is there evidence that bioconcentration is an important factor in aluminum toxicity (see Section 3.3). As well, all the LOEC data at pH 4.5 to 5.5 are within a narrow range, therefore the criterion can be calculated using a safety factor of 0.5 and the LOEC of the most sensitive species and life stage, i.e. $0.5 \times 0.030 \text{ mg/L} = 0.015 \text{ mg/L}$.

Table 5.1: Highest No Observed Effect Concentration (NOEC) and Lowest Observed Effect Concentration (LOEC) Data (mg/L) used for Aluminum Criteria Development.

<u>pH 4.5-6.5 groups</u>	<u>Highest NOEC</u>	<u>LOEC(Inorg. Al)¹</u>	<u>LOEC (IMAL)²</u>
Eggs	-	0.060 (pH=5.6)	0.018 (pH=6.0)
Fry	0.010 ² (pH=4.5 & 5.5)	0.050 (pH=5.4)	0.030 (pH=4.8)
Fingerlings, juveniles, adults	0.045 ¹ (pH=6.1)	0.062 (pH=4.8)	0.051 (pH=5.5)
Sublethal effects	0.019 ¹ (pH=4.5 & 5.5)	0.038 (pH=4.5 & 5.5)	0.038 (pH=4.5 & 5.5)
<u>pH >6.5-9.0</u>	<u>NOEC</u>	<u>LOEC ([Al]³)</u>	
	0.060 ³ (pH=7.6)	0.150 (pH=6.9 & 7.4)	

Footnotes.

1. Acid soluble inorganic aluminum excluding any clay fraction.
2. Inorganic monomeric aluminum.
3. Total aluminum, excluding any clay fraction.

THE CRITERION FOR pH 4.5 to 5.5 = 0.015 mg/L BASED ON
INORGANIC MONOMERIC ALUMINUM (AS DEFINED IN SECTION 2.2)
MEASURED IN CLAY-FREE SAMPLES.

This value is below the threshold chronic toxicity value (the geometric mean of the LOEC and NOEC of the most sensitive species and lifestage, i.e. 0.017 mg/L) but above the NOEC value of 0.010 mg/L.

If this criterion is exceeded in any water body unaffected by man-made inputs with a natural pH level of 4.5 to 5.5 no condition of aluminum is permitted that would increase the average natural background inorganic monomeric aluminum concentration by more than 10%.

As the inorganic aluminum species data was only available for fish this criterion must be classed as a Provincial Water Quality Guideline, rather than a PWQ Objective. The latter would require the availability of toxicological data for a wide range of aquatic life including invertebrates and algae or aquatic plants.

5.1.2 pH >5.5-6.5

At present it is not possible to calculate a numerical guideline for acid soluble inorganic aluminum at pH >5.5 to 6.5. If the same rationale as that discussed above could be used for this pH range the criterion could be calculated from the data shown in Table 5.1 as 0.015 mg/L, i.e. 0.25 (a larger safety factor is used because of the smaller amount of data) x 0.060 mg/L (the lowest LOEC based on acid soluble inorganic aluminum for this pH range). However, the precise nature of the toxic species of inorganic aluminum at pH >5.5 to 6.5 has not yet been determined. It is probable that only the smaller polymeric or colloidal forms of acid soluble inorganic aluminum are toxic to aquatic organisms, and at present these forms cannot be chemically differentiated from larger acid soluble inorganic

In lieu of a specific numerical objective or guideline for aluminum in this pH range, the Ministry of the Environment recommends:

IN WATER BODIES WHERE pH IN THE RANGE >5.5 TO 6.5 UNITS IS ENCOUNTERED, NO CONDITION SHOULD BE PERMITTED WHICH WOULD INCREASE THE ACID SOLUBLE INORGANIC ALUMINUM CONCENTRATION IN A FILTERED (CLAY-FREE) SAMPLE MORE THAN 10% ABOVE BACKGROUND CONCENTRATIONS FOR WATERS REPRESENTATIVE OF THAT GEOLOGICAL AREA OF THE PROVINCE.

Average background concentrations should be established at locations that are relatively unaffected by anthropogenic sources and that are known to support normal aquatic communities. For the purpose of this guideline it is assumed that organisms are acclimated to natural background concentrations or, in fact, such concentrations are no effect levels. If there is an indication of organism stress that might be related to the presence of aluminum, this background concentration should not be used.

It must be stressed that the aluminum analysis for waterbodies in the >5.5 to 6.5 unit pH range is of filtered (clay-free) acid soluble inorganic aluminum. A total aluminum value is not appropriate. Although an increase of 10% above natural background levels is an arbitrary guideline, it is based as closely as possible on current knowledge. Typical natural acid soluble inorganic aluminum levels in waters in the >5.5 to 6.5 pH range are <0.100 mg/L. 10% of this value is 0.010 mg/L and this is relatively comparable to the 0.015 mg/L value calculated as being an approximation of a no significant adverse effect concentration.

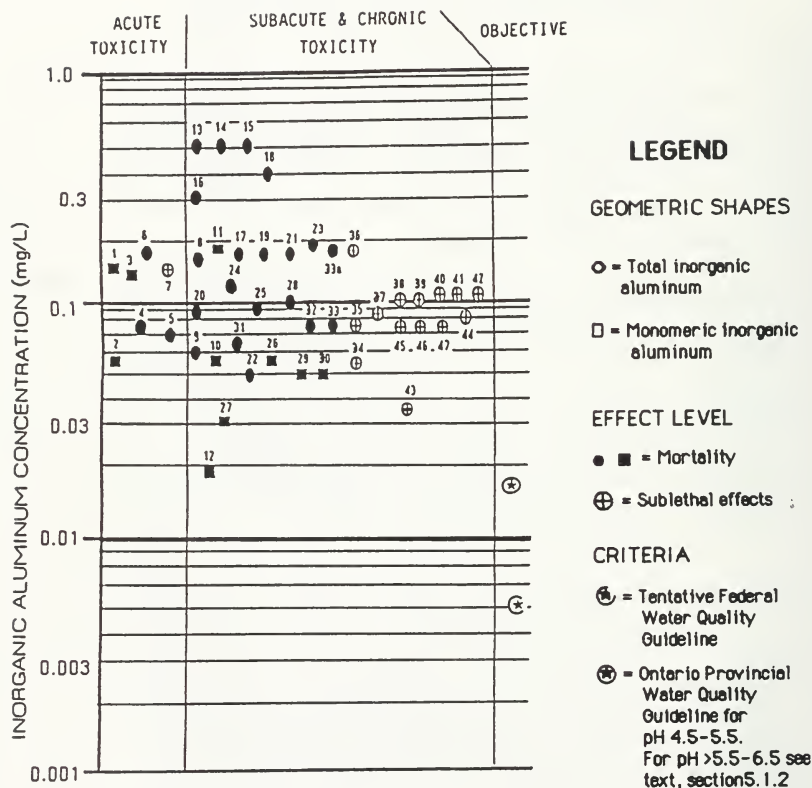


FIGURE 5.1

Summary of Aquatic Effects and Criteria at pH 4.5 - 6.5

Continuation of legend for Figure 5.1

No.	Species ¹	Stage ² Life	Duration	Reference
1.	Ss	J-A	60h	Rosseland & Skogheim, 1982
2.	"	A	36h	" " " " , 1984
3.	"	"	"	Skogheim et al., 1984
4.	Sg	J-A	2-4d	Neville, 1985
5.	Nc	A	7h	Kramer et al., 1986
6.	"	"	"	" " " "
7.	Ss	J-A	3d	Rosseland & Skogheim, 1982
8.	Cc	Eggs	3w	Baker & Schofield, 1982
9.	"	"	"	" " " "
10.	"	"	14d	Holtze et al. In preparation.
11.	Sv	"	22d	" " " "
12.	Nc	"	9d	" " " "
13.	Sg	"	8d + 12d recovery	Holtze, 1983
14.	"	"	"	Baker & Schofield, 1982
15.	Sf	Fry	2w	" " " "
16.	"	"	"	" " " "
17.	"	"	"	" " " "
18.	"	"	"	" " " "
19.	"	"	"	" " " "
20.	Cc	"	"	" " " "
21.	"	"	"	" " " "
22.	"	"	"	" " " "
23.	"	"	"	" " " "
24.	"	"	"	" " " "
25.	"	"	"	" " " "
26.	"	"	18d	Holtze et al. In preparation.
27.	Sv	"	26d	" " " "
28.	Sg	"	8d	Holtze, 1983.
29.	Sn	"	5d	Gunn & Keller, 1984
30.	"	"	"	" " " "
31.	St	Fing.	6w	Sadler & Lynam, 1986
32.	"	"	"	" " " "
33.	Sg	J-A	5-7d	Neville, 1985
33a.	"	Fing.	5d	Orr et al., 1986
34.	Ss	J-A	6d	Henriksen et al., 1984
35.	"	Fry	30-60d	Jagoe et al., 1987
36.	Sf	"	14d	Baker & Schofield, 1982
37.	"	"	"	" " " "
38.	"	"	"	Schofield & Trojnar, 1980
39.	"	"	"	" " " "
40.	Cc	"	"	Baker & Schofield, 1982
41.	"	"	"	" " " "
42.	Sn	"	5d	Gunn, 1987
43.	St	Fing.	6w	Sadler & Lynam, 1986
44.	"	"	"	" " " "
45.	Sg	J-A	11d	Neville, 1985
46.	"	"	6d	" " " "
47.	"	"	11d	" " " "

Footnotes: ¹See Figures 4.4-4.7 for full species names.

²J-A = Juveniles - Adults
A = Adults
Fing. = Fingerlings

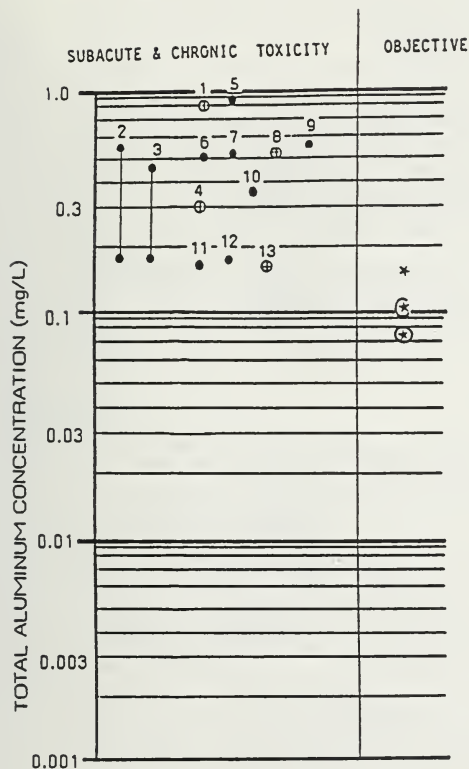
5.2 pH range >6.5-9.0

The aluminum criterion for pH >6.5 to 9.0 is developed from the data described in Section 4.5 and shown in Table 4.1, Fig. 4.8 and Fig. 5.2. Identification of the toxic aluminum species in this pH range is even more imprecise than in the mildly acidic pH range discussed above (Section 5.1.2). All the data are based on total aluminum concentrations and may include dissolved and suspended inorganic and organic species. Current routine analytical procedures do not separate these forms. However, the data clearly show the toxicity of total aluminum at concentrations <1 mg/L.

There appears to be no direct relationship between pH and aluminum toxicity from pH >6.5 to 7.8 (see Fig. 4.8), and there is insufficient data to show whether or not such a relationship exists from pH 7.9 to 9.0. Therefore, at present, a single aluminum criterion has been developed for this pH range. The LOEC is 0.150 mg/L total aluminum (7 day EC₅₀ for goldfish embryos and fry, and gill deformity and increased opercular movement in brown trout yearlings) (see Table 5.1). The highest NOEC is 0.060 mg/L total aluminum (survival of lake trout sac fry). In both cases "total aluminum" excludes any clay fraction.

Using the same rationale as that discussed in Section 5.1 the criterion can be calculated using a safety factor of 0.5 and the lowest observed effect concentration, i.e. $0.5 \times 0.150 \text{ mg/L} = 0.075 \text{ mg/L}$.

THE CRITERION FOR TOTAL ALUMINUM AT pH >6.5 to 9.0 = 0.075 mg/L, BASED ON TOTAL ALUMINUM CONCENTRATIONS MEASURED IN CLAY-FREE SAMPLES.



LEGEND

EFFECT LEVEL

- = Mortality
- ⊗ = Sublethal effects

CRITERIA

- * = USEPA Objective (4d average)
- ⊗ = Tentative Federal Water Quality Guideline
- ⊗ = Ontario Provincial Water Quality Guideline

#	SPECIES ¹	DURATION
1.	Cm	8d
2.	Sc	4d
3.	-	-
4.	Dm	21d
5.	Td	55d
6.	Sg	8d+ 12d recovery
7.	-	44d
8.	-	-
9.	-	28d
10.	-	-
11.	Ce	7d
12.	Ms	8d
13.	St	10m

Footnote:

1. See Table 4.1 for full species name and references.

FIGURE 5.2
Summary of Aquatic Effects and
Criteria at pH > 6.5 - 9.0

This value is below the threshold chronic toxicity value, (the geometric mean of 0.150 and 0.060 mg/L, i.e. 0.095 mg/L) but above the NOEC value of 0.060 mg/L.

If this criterion is exceeded in any water body unaffected by man-made inputs with a natural pH level of >6.5 to 9.0 that supports a normal aquatic community, no condition is permitted that would increase the average natural background total aluminum concentration in clay-free samples by more than 10%.

N.B. A new data base for background levels must be established as previous data was measured in unfiltered samples. (See Appendix I for new analytical procedures).

5.3 Criteria of other agencies

The only other criterion for aluminum in acid environments (pH <6.5) is 0.005 mg/L total aluminum for the protection of freshwater aquatic life developed by the Canadian Council of Resource and Environment Ministers for the Federal Government. It is classified as a tentative guideline because it was developed while much of the recently published data on the toxicity of various forms of aluminum was just becoming available. The guideline is for total aluminum concentrations and therefore does not take into account the effect of any complexing ligands. It was based on NOEC data for the American toad at pH 4.3. The Ontario criteria for acid environments cover only the pH range 4.5 to 6.5 because aluminum has been shown to be less toxic than hydrogen ions at pH levels below 4.5 for the majority of species tested.

For the pH range >6.5 the Canadian Federal Government has adopted the guideline proposed by U.S. EPA in 1973, i.e. 0.100 mg/L total aluminum. This is also a tentative guideline to be

used until further data showing the effects of complexing ligands on aluminum toxicity can be taken into account. There is no specification that this guideline is to be used in clay-free samples. The latest objective published by U.S. EPA in 1986, based on total acid soluble aluminum (i.e. including inorganic and organic forms of acid soluble aluminum, but excluding clay fractions) is 0.150 mg/L. This is the maximum allowable 4 day average that can occur in a 3 year period. Unlike Ontario objectives, U.S. EPA objectives are not designed to protect the most sensitive species and life stage of aquatic organisms. For instance, the concentration of aluminum in their present objective equals the lowest observed effect concentration in the data reported in this document for this pH range (see Table 4.1)

5.4 Recommended Research

- i. Methodology should be developed to routinely measure the toxic forms of aluminum at pH >5.5 to 6.5, and >6.5 to 9.0 in clay-free samples.
- ii. The toxicity of organic forms of aluminum of pH >6.5 to 9.0 should be studied. If found to be non-toxic, methodology should be developed to routinely separate organic and inorganic forms of aluminum at concentrations <1 mg/L.
- iii. The toxic component of aluminum in low supersaturated concentrations of acid soluble inorganic aluminum at pH >5.5 to 6.5 should be identified.
- iv. Studies of the toxicity of monomeric and acid soluble forms of inorganic aluminum at pH 4.5 to 6.5 on aquatic biota other than fish are needed.

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APPENDIX I

ANALYTICAL METHODS

Analytical methods can be divided into those which measure "total" aluminum in water and those which measure some fraction of the total ("speciation"). However, even those methods which purport to measure "total" aluminum may do so in varying degrees.

One major group of "total" methods uses acid digestion to solubilize the aluminum (into Al^{3+}) before complexation by an organic reagent and subsequent analysis. Although the details of acid digestion vary from method to method, they are all presumably complete with respect to particulate and colloidal aluminum hydroxides; aluminum from clays, however, would not usually be solubilized. In waters with a high refractory organic matter content, a UV digestion may also be required (Campbell et al. 1983).

Following digestion, the complexation of aluminum with 8-hydroxyquinoline (Oxine) at pH 8 and extraction into methylisobutylketone, benzene or chloroform (Barnes 1975; Burrows 1977) can achieve a detection limit of 0.01 to 0.05 mg Al/L with flame atomic absorption spectrophotometry (AAS). Graphite furnace atomization (GFAAS) may be necessary to enhance the detection limit of this method (LaZerte 1984). A colorimetric procedure uses a similar complexing reagent (Ferron), with orthophenanthroline to suppress iron interference; however it is much less sensitive. A very sensitive method using the fluorimetric dye Lumogallion as complexing reagent is also available (Hydes and Liss 1976). These last two methods are rarely employed, however, as a simpler, interference free, and sufficiently sensitive colorimetric procedure which uses catechol violet as the complexing reagent (Dougan and Wilson 1974) is available and easily automated. Depending upon cuvette length, detection limits down to 2 $\mu g/L$ are possible with this method (LaZerte et al. 1988).

Direct GFAAS and plasma emission spectrophotometry are also commonly employed. These are a more complete "total" than any of the previous methods dependent upon acid digestion (possibly followed by extraction) as some fraction of any suspended clays and any refractory organic matter will be broken down at the high temperatures employed.

A separation of particulate from non-particulate (or filterable) aluminum requires filtration (usually with a 0.45 μm polycarbonate filter) and analysis of the filtrate by any of the "total" methods described above. Frequently, however, filtration is dropped in favor of one of the speciation methods outlined below, especially when the amount of suspended clay is low.

Many of the "total" methods employing an organic complexing reagent after acid/uv digestion have also been used without any prior digestion or filtration. The results are necessarily quite variable and dependent upon reaction reagent concentrations, temperature, duration of the reaction and pH. For example, LaZerte (1984), following Turner (1969), used a 15 s oxine extraction to estimate "fast reactive Al" and a 3-6 h extraction to estimate a "total reactive Al", the difference between the two fractions was thought to be polymeric aluminum with the "fast reactive aluminum" roughly corresponding to inorganic monomeric plus organic aluminum. Others have used pH shifts with oxine to attempt a separation of the aluminum fluoride complexes from other inorganic monomeric forms (James et al. 1983). Relative rates of reaction have also been used to separate different polymeric forms (Smith and Hem 1972) as well as organic from inorganic monomeric aluminum (Kramer et al., 1981).

In general though, most of these methods provide an aluminum fraction which can be interpreted as the inorganic monomeric fraction plus (most of) the organic aluminum, and excluding (most of) the polymeric, colloidal and solid fraction (Fig. 2.1). The terminology for this fraction includes "reactive", "labile" and "total monomeric" aluminum. The "total monomeric" terminology of Driscoll (1984) has gained the

widest acceptance. It has been shown by Seip et al. (1984) that this "total monomeric" fraction estimated by the catechol violet method is equivalent to that estimated by the oxine extraction method. A recent laboratory intercomparison study (Aspilla 1987) also supports this contention.

The difference between "total monomeric" and an acid digested "total" is usually referred to as the "acid soluble" fraction, which should include polymeric, colloidal and particulate (if unfiltered) aluminum hydroxides (Fig. 2.1).

Given an estimate of "total monomeric" aluminum, most aluminum speciation schemes then proceed to physically separate this fraction into organic and inorganic monomeric forms using dialysis or cation exchange (Fig. 2.1). Other approaches have only rarely been used. Equilibrium dialysis allows the penetration of low molecular weight inorganic monomeric species through a 1000 mwco dialysis tube which contains high purity water. After equilibration, the dialyzate is removed and analyzed (LaZerte 1984). To avoid dialysis of small organic complexes, dialysis time is minimized to that necessary for the almost complete equilibration of inorganic monomeric forms.

Alternatively, cation exchange or chelation resins can be used to measure the organic monomeric fraction (Campbell et al. 1983; Driscoll 1984; LaZerte et al., 1988). When a sample aliquot exchanges with the resin, all of the positively charged inorganic aluminum forms are absorbed leaving the negatively charged organic fraction behind. To reduce possible stripping of aluminum from the organic fraction, contact time with the resin is kept to the minimum necessary for inorganic aluminum adsorption. The inorganic monomeric aluminum fraction is calculated by subtracting the organic monomeric fraction from total monomeric aluminum. This method is only applicable at pH's less than about 6.5 where the inorganic fraction is dominated by positively charged monomers (see section 2.2). When neutral or negatively charged monomers (at pH's greater than 6.5) or positively charged polymers exist (neutralizing conditions), the method will be in error. Under these conditions, the dialysis method is preferable.

Although these speciation methods can best be described as operational, encouraging evidence exists that they do indeed measure what they are intended to measure. Part of the evidence comes from a method as yet undescribed. The free/total fluoride procedure uses the measurement of free (F^-) and total fluoride, along with the assumption that the difference is due solely to aluminum fluorides, to calculate the inorganic monomeric fraction of aluminum. The method is not common because of the time consuming nature of the free fluoride estimate, and its potential inaccuracies at higher pH's ($pH \geq 5.0$; LaZerte 1984) and low fluoride levels. Nonetheless it does provide an estimate of inorganic monomeric aluminum, that is totally independent of any direct aluminum measurements. LaZerte (1984) has compared the dialysis speciation and others (Driscoll 1984; Schofield 1984) have compared the ion exchange procedure with the total/free fluoride methods. In both cases, good to excellent correspondence was found: the methods were within 15% of each other. To complete the intercomparison, LaZerte et al. (1988) have compared the dialysis with the ion exchange procedure. The correspondence was excellent: within $\pm 1\%$ of each other.

For the pH range 4.5-5.5, inorganic monomeric aluminum can be estimated using the automatic method described in LaZerte et al., (1988).

For the pH range 5.5-6.5, inorganic aluminum includes inorganic monomeric aluminum plus acid soluble aluminum, but excludes organic monomeric and any clay fraction. If it is known that a water sample contains a negligible amount of suspended clays, then a GFAAS or ICP "total" minus the organic monomeric fraction provided by the LaZerte et al., (1988) method will give an estimate of inorganic aluminum so defined. However, if suspended clays are present, the sample should be allowed to settle and the supernatant filtered (0.45μ or preferably less, e.g. 0.2μ), and perhaps a less destructive "total" (Dougan and Wilson 1974) might be more appropriate. The same considerations apply to the definition of "total" aluminum used in the pH range 6.5-9.0, except that the estimation and subtraction of organic monomeric aluminum is not required.

Note:

Field samples collected for aluminum speciation are not stable. An increase in temperature can induce over-saturation and precipitation of those samples close to saturation (Seip et al. 1984); similarly, CO₂ degassing can occasionally induce sufficient pH elevation for over-saturation and precipitation (C. Driscoll, Syracuse Univ., pers. communication). Samples collected for aluminum speciation should be analyzed immediately if possible, and refrigerated until analysis if not.

APPENDIX II

PROBLEMS IN INTERPRETATION OF "BIOACCUMULATION" DATA

The potential for bioaccumulation of aluminum by aquatic organisms is a function of the concentration in water, the chemical speciation and bioavailability, and the food chain dynamics (i.e. biomagnification). The bioconcentration factor (i.e. the concentration in the organism compared to that in the water) can be calculated from the tissue and ambient water concentrations as follows:-

$$\text{BCF} = \frac{\text{Concentration in aquatic organism } (\mu\text{g/g wet weight})}{\text{Concentration in water } (\text{mg/L})}$$

When using the equation it is assumed that the water concentration is relatively stable, and that the concentration in the organism is in equilibrium with that in the water. The first assumption is difficult to ensure in field studies, and the second often necessitates expensive long term, flow through studies in the laboratory. Interpretation of BCF data is also difficult unless the mechanism of toxicity and the target organ concentration at which adverse effects occur are known. Table A II shows estimated "BCF" values for various species calculated from data reported in the literature, though not all of the studies were designed to calculate bioconcentration values. The footnotes include information and interpretation outlined by the author. Ambient pH values were between 6.3 and 9.0. The organisms used were apparently unaffected by the aluminum except for the brown trout collected from a trout farm supplied by water from a limed "acid lake" (see Karlsson-Norrgrén, 1986, footnote #13) which showed "increased frequency of opercular movement and, in some cases, skin darkening".

None of the estimates fulfill the requirements outlined above. In many cases, problems with the data used include:

- 1) the uncertainty of ambient aluminum concentrations, some of which are single mid-lake values, others are mean annual values, and the inclusion of organic forms of aluminum which are probably not toxic (see section 4).
- 2) the incomplete whole body tissue concentrations, since some data are taken from tests designed to show target organs and individual organ bioconcentration values.

Nevertheless, many of the data show a lack of aluminum uptake from the water column (see footnote #5 in Table A II. Malley et al. (1987) found that the tissue aluminum concentration decreased when crayfish from a low aluminum lake (0.036 mg/L) were transferred to a high aluminum exposure tank (0.500 mg/L) without feeding, for 14d, and in two other studies tissue aluminum concentrations were higher in fish from lakes with no measurable aluminum in the water column than in fish from lakes with 0.100 and 0.320 mg/L aluminum in the water column (Buerger and Soltero, 1983; Berg and Burns, 1985). These studies indicate that when the aluminum concentration in gill tissue is less than that in other tissues, the aluminum is more likely to have accumulated from the sediments or from food rather than from the water column.

"BIOACCUMULATION"

Table A II

Species	Ambient Water Al conc. (mg/L)	Ambient pH	Tissue Al conc. (µg/g wet weight)	"BCF" Calculation	Source
<u>Euglena gracilis</u>	0.210 ¹		190 ²	905	Cowgill and Burns, 1975
<u>Daphnia magna</u>	"		110 ^{2, 3}	524	"
<u>Daphnia pulex</u>	"		120 ^{2, 3}	571	"
<u>Orconectes virilis</u>	0.036	6.7	47 ⁴	1,305 ⁵	Malley et al. 1987
" "	0.500 ⁶	"	37 ⁴	74	"
<u>Salmo gairdneri</u>	0.320 ⁷	~9.1	3.06 ^{8, 9}	9.6	Buergel and Soltero, 1983
" "	<0.001 ¹⁰		3.2 ^{8, 9}	- ⁵	"
<u>Perca flavescens</u>	0.030 ¹¹	7.4	6.0 ²	200	Suns, 1985
<u>Salmo trutta</u>	0.016 ¹⁰	6.3 -6.9	9.5 ¹²	594	Karlsson- Norrgrén, 1986
" "	0.137 ¹³ -0.150 (labile inorganic Al = 0.027-0.012)	"	45 ¹²	328 (1,661) ¹⁴	"
<u>Ictalurus punctatus</u>	0.100 ¹⁵	7.8	572 ¹⁶	5720 ⁵	Berg and Burns, 1985
" "	0 ¹⁰	"	1095 ¹⁶	- ⁵	"
<u>Dorosoma cepedianum</u>	0.100 ¹⁵	"	748 ¹⁶	7480 ⁵	"
<u>Micropterus salmoides</u>	"	"	701 ¹⁶	7010 ⁵	"

Table A II Cont'd.....

Footnotes:

- ¹"Spring water" - high concentration of dissolved solids
- ²Whole body tissue concentration
- ³Aluminum in daphnids probably accumulated from food (Euglena gracilis) and water and may have adhered to body surface. Data indicate that biomagnification did not occur.
- ⁴All tissues except for gut.
- ⁵Aluminum presumably accumulated from food or sediments, (see footnote #6 and 15).
- ⁶Laboratory exposure of crayfish from the same lake as that shown above to 0.500 mg/L aluminum for 14 d without feeding. Loss of aluminum from the tissues (compared to values shown above) despite the high aluminum concentration in the exposure medium implies that aluminum is absorbed into crayfish from food or sediments rather than from the water.
- ⁷Fish stocked in previously limed "acid lake". Tissue aluminum values were similar to those in fish from a lake with no measurable dissolved aluminum in the water column.
- ⁸Dry weight reported in literature presumed to be 20% of wet weight.
- ⁹Tissues include liver, kidney, stomach, muscle, gill, heart, and reproductive organs.
- ¹⁰Control lake.
- ¹¹Approximate average lake concentrations (La Zerte, pers. comm.)
- ¹²Tissues include liver, kidney, intestine, muscle, bone and gill.
- ¹³Fish from trout farm supplied by water from a limed "acid lake".
- ¹⁴"BCF" for "labile inorganic aluminum" only.
- ¹⁵Fish from a lake receiving alum sludge from a water treatment plant, pH 7-8. Lake water aluminum concentrations measured on one surface water sample. There is no evidence of increased tissue aluminum concentration compared to data from a nearby control lake where no dissolved aluminum was found in the surface water.
- ¹⁶Tissues include liver, kidney, brain, gill and muscle.

